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(54) LIQUID INK CONTAINING SURFACE TREATED COLORANT AND ITS MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a liquid ink containing colorant particles which have been surface-treated with a polymer having a unit to be derived from at least one nitrogen-containing polymerizable monomer, and its manufacturing method.

SOLUTION: The liquid ink comprises a carrier liquid, an organosol, and a colorant which has been surface-treated with a polymer having a unit to be derived from at least one nitrogen-containing polymerizable monomer. By containing the colorant which has been surface-treated with a polymer having a unit to be derived from at least one nitrogen-containing polymerizable monomer, the liquid ink which has improved charge-formability and reduced conductivity variation, and improved dispersion stability can be obtained.

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(54) 【発明の名称】 表面処理された着色剤を含む液体インキ及びその製造方法

(57) 【要約】

【課題】 少なくとも一つの窒素含有重合性モノマーから誘導されるユニットを含むポリマーで表面処理された着色剤粒子を含有している液体インキ及びその製造方法を提供する。

【解決手段】 上記液体インキはキャリア液体、オルガノソル及び、少なくとも一つの窒素含有重合性モノマーから誘導されるユニットを含むポリマーで表面処理された着色剤を含むことを特徴とする。これにより、少なくとも一つの窒素含有重合性モノマーから誘導されるユニットを含むポリマーで表面処理された着色剤を含むことによって、改善された電荷形成能力と減少した伝導度変動性及び改善された分散安定性を有する液体インキが得られる。

【特許請求の範囲】

【請求項1】 キャリア液体と、オルガノゾルと、少なくとも一つの窒素含有重合性モノマーから誘導されるユニットを含むポリマーで表面処理された着色剤と、を含むことを特徴とする液体インキ。

【請求項2】 前記着色剤は、表面のコーティング又は化学的改質方式によって表面処理された顔料である、ことを特徴とする請求項1に記載の液体インキ。

【請求項3】 前記キャリア液体は、脂肪族炭化水素、脂環族炭化水素、芳香族炭化水素、ハロゲン化された炭化水素溶媒、シリコンオイル類及びこれら混合物からなり、カウリープタノール数値が30未満である、ことを特徴とする請求項1に記載の液体インキ。

【請求項4】 前記液体インキは、さらに電荷ディレクタを含む、ことを特徴とする請求項1に記載の液体インキ。

【請求項5】 前記電荷ディレクタは、多価金属イオン及びカウンタイオンである有機陰イオンより構成された金属塩であると共に、前記多価金属イオンは、Ba(II)、Ca(II)、Mn(II)、Zn(II)、Zr(IV)、Cu(II)、Al(III)、Cr(III)、Fe(II)、Fe(III)、Sb(III)、Bi(III)、Co(II)、La(III)、Pb(II)、Mg(II)、Mo(III)、Ni(II)、Ag(I)、Sr(II)、Sn(IV)、V(V)、Y(III)、Ti(IV)からなる群から選択された1以上であり、かつ、前記有機陰イオンは、脂肪族カルボン酸及び芳香族カルボン酸のうちいずれか一つから誘導されるカルボキシレート又は脂肪族スルホン酸及び芳香族スルホン酸から選択された一つから誘導されるスルホン酸塩である、ことを特徴とする請求項4に記載の液体インキ。

【請求項6】 前記窒素は、アミド(amide)、アミド(amido)、アミノ及びアミングループからなる群から選択されたグループに存在する、ことを特徴とする請求項1に記載の液体インキ。

【請求項7】 前記窒素含有重合性モノマーは、脂肪族アミノラジカルを有するメタクリレート又はアクリレート、窒素含有ヘテロ環ビニールモノマー、N-ビニール置換された環状のアミドモノマー、(メタ)アクリルアミドモノマー、窒素ラジカル含有芳香族置換されたエチレンモノマー及び窒素含有ビニールエーテルモノマーからなる群から選択された1以上である、ことを特徴とする請求項1に記載の液体インキ。

【請求項8】 前記脂肪族アミノラジカルを有するメタクリレート又はアクリレートは、N、N-ジメチルアミノエチル(メタ)アクリレート、N、N-ジエチルアミノエチル(メタ)アクリレート、N、N-ジブチルアミノエチル(メタ)アクリレート、N、N-ヒドロキシエチルアミノ(メタ)アクリレート、N-ベンジル-N

-エチルアミノ(メタ)アクリレート、N、N-ジベンジルアミノエチル(メタ)アクリレート及びN-オクチル、N、N-ジヘキシルアミノエチル(メタ)アクリレートからなる群から選択された1以上であり、前記窒素含有ヘテロ環ビニールモノマーは、N-ビニールイミダゾール、N-ビニールインダゾール、N-ビニールテトラゾール、2-ビニールピリジン、4-ビニールピリジン、2-メチル-5-ビニールピリジン、2-ビニールキノリン、4-ビニールキノリン、2-ビニールピラジン、2-ビニールオキサゾール、2-ビニールベンゾオキサゾールからなる群から選択された1以上であり、前記(メタ)アクリルアミドモノマーは、N-メチルアクリルアミド、N-オクチルアクリルアミド、N-フェニルメタアクリルアミド、N-シクロヘキシルアクリルアミド、N-フェニルエチルアクリルアミド、N-p-メトキシフェニルアクリルアミド、アクリルアミド、N、N-ジメチルアクリルアミド、N、N-ジブチルアクリルアミド、N-メチル、N-フェニルアクリルアミドからなる群から選択された1以上であり、前記N-ビニール置換された環状のアミドモノマーは、N-ビニールピロリドン、N-ビニールピペリドン、N-ビニールオキサゾリドンからなる群から選択された1以上であり、前記窒素ラジカル含有芳香族置換されたエチレンモノマーは、ジメチルアミノスチレン、ジエチルアミノスチレン、ジエチルアミノメチルスチレン、ジオクチルアミノスチレンからなる群から選択された1以上であり、前記窒素含有ビニールエーテルモノマーは、ビニール-N-エチル-N-フェニルアミノエチルエーテル、ビニール-N-ブチル-N-フェニルアミノエチルエーテル、トリエタノールアミンジビニールエーテル、ビニールジフェニルアミノエチルエーテル、ビニールピロリジルアミノエーテル、ビニール-β-モルホリノエチルエーテル、N-ビニールヒドロキシエチルベンズアミド、m-アミノフェニルビニールエーテルからなる群から選択された1以上である、ことを特徴とする請求項7に記載の液体インキ。

【請求項9】 前記ポリマーの重量平均分子量は、50,000から150,000ダルトンである、ことを特徴とする請求項1に記載の液体インキ。

【請求項10】 前記着色剤は、カーボンブラック顔料である、ことを特徴とする請求項1に記載の液体インキ。

【請求項11】 (a-1) 少なくとも一つの窒素含有重合性モノマーから誘導されるユニットを含むポリマーを溶媒に溶解してポリマー溶液を形成する段階と、(b-1) 着色剤粒子を前記ポリマー溶液に分散して着色剤分散液を形成する段階と、(c-1) 前記着色剤分散液から少なくとも若干の溶媒を除去して処理された着色剤粒子を形成する段階と、(d-1) 前記処理された着色剤をキャリア液体含有オルガノゾルに分散させる段階

と、を含むことを特徴とする液体インキの製造方法。

【請求項12】 前記窒素含有重合性モノマーでの窒素原子は、アミド (amide)、アミド (amido)、アミノ及びアミングループからなる群から選択されたグループに存在する、ことを特徴とする請求項11に記載の液体インキの製造方法。

【請求項13】 前記窒素含有重合性モノマーは、脂肪族アミノラジカルを有するメタクリレート又はアクリレート、窒素含有ヘテロ環ビニールモノマー、N-ビニール置換された環状のアミドモノマー、(メタ)アクリルアミドモノマー、窒素ラジカル含有芳香族置換されたエチレンモノマー及び窒素含有ビニールエーテルモノマーからなる群から選択された1以上である、ことを特徴とする請求項11に記載の液体インキの製造方法。

【請求項14】 前記脂肪族アミノラジカルを有するメタクリレート又はアクリレートは、N、N-ジメチルアミノエチル(メタ)アクリレート、N、N-ジエチルアミノエチル(メタ)アクリレート、N、N-ジブチルアミノエチル(メタ)アクリレート、N、N-ヒドロキシエチルアミノ(メタ)アクリレート、N-ベンジル-N-エチルアミノ(メタ)アクリレート、N、N-ジベンジルアミノエチル(メタ)アクリレート及びN-オクチル、N、N-ジヘキシルアミノエチル(メタ)アクリレートからなる群から選択された1以上であり、前記窒素含有ヘテロ環ビニールモノマーは、N-ビニールイミダゾール、N-ビニールインダゾール、N-ビニールテトラゾール、2-ビニールピリジン、4-ビニールピリジン、2-メチル-5-ビニールピリジン、2-ビニールキノリン、4-ビニールキノリン、2-ビニールピラジン、2-ビニールオキサゾール、2-ビニールベンゾオキサゾールからなる群から選択された1以上であり、前記(メタ)アクリルアミドモノマーは、N-メチルアクリルアミド、N-オクチルアクリルアミド、N-フェニルメタアクリルアミド、N-シクロヘキシルアクリルアミド、N-フェニルエチルアクリルアミド、N-p-メトキシフェニルアクリルアミド、アクリルアミド、N、N-ジメチルアクリルアミド、N、N-ジブチルアクリルアミド、N-メチル、N-フェニルアクリルアミドからなる群から選択された1以上であり、前記N-ビニール置換された環状のアミドモノマーは、N-ビニールピロリドン、N-ビニールピペリドン、N-ビニールオキサゾリドンからなる群から選択された1以上であり、前記窒素ラジカル含有芳香族置換されたエチレンモノマーは、ジメチルアミノスチレン、ジエチルアミノスチレン、ジエチルアミノメチルスチレン、ジオクチルアミノスチレンからなる群から選択された1以上であり、及び前記窒素含有ビニールエーテルモノマーは、ビニール-N-エチル-N-フェニルアミノエチルエーテル、ビニール-N-ブチル-N-フェニルアミノエチルエーテル、トリエタノールアミンジビニールエーテル、ビニ

ールジフェニルアミノエチルエーテル、ビニールピロリジルアミノエーテル、ビニール-β-モルホリノエチルエーテル、N-ビニールヒドロキシエチルベンズアミド、m-アミノフェニルビニールエーテルからなる群から選択された1以上である、ことを特徴とする請求項13に記載の液体インキの製造方法。

【請求項15】 前記(b-1)段階で得られた分散液は、電荷ディレクタをさらに含む、ことを特徴とする請求項11に記載の液体インキの製造方法。

【請求項16】 前記(a-1)段階での溶媒のカウリーブタノール数値が30以上である、ことを特徴とする請求項11に記載の液体インキの製造方法。

【請求項17】 前記(d-1)段階でのキャリア液体のカウリーブタノール数値が30未満である、ことを特徴とする請求項11に記載の液体インキの製造方法。

【請求項18】 前記着色剤は、カーボンブラック顔料である、ことを特徴とする請求項11に記載の液体インキの製造方法。

【請求項19】 (a-2)少なくとも一つの窒素含有重合性モノマーから誘導されるユニットを含むポリマーを溶媒に溶解してポリマー溶液を形成する段階と、(b-2)着色剤粒子を前記ポリマー溶液に分散して着色剤分散液を形成する段階と、(c-2)前記着色剤分散液から処理された着色剤粒子を沈積させる段階と、(d-2)前記処理された着色剤粒子をキャリア液体含有オルガノゾルに分散させる段階と、を含むことを特徴とする液体インキの製造方法。

【請求項20】 前記窒素は、アミド (amide)、アミド (amido)、アミノ及びアミングループからなる群から選択されたグループに存在する、ことを特徴とする請求項19に記載の液体インキの製造方法。

【請求項21】 前記窒素含有重合性モノマーは、脂肪族アミノラジカルを有するメタクリレート又はアクリレート、窒素含有ヘテロ環ビニールモノマー、N-ビニール置換された環状のアミドモノマー、(メタ)アクリルアミドモノマー、窒素ラジカル含有芳香族置換されたエチレンモノマー及び窒素含有ビニールエーテルモノマーからなる群から選択された1以上である、ことを特徴とする請求項19に記載の液体インキの製造方法。

【請求項22】 前記脂肪族アミノラジカルを有するメタクリレート又はアクリレートは、N、N-ジメチルアミノエチル(メタ)アクリレート、N、N-ジエチルアミノエチル(メタ)アクリレート、N、N-ジブチルアミノエチル(メタ)アクリレート、N、N-ヒドロキシエチルアミノ(メタ)アクリレート、N-ベンジル-N-エチルアミノ(メタ)アクリレート、N、N-ジベンジルアミノエチル(メタ)アクリレート及びN-オクチル、N、N-ジヘキシルアミノエチル(メタ)アクリレートからなる群から選択された1以上であり、前記窒素含有ヘテロ環ビニールモノマーは、N-ビニールイミ

ダゾール、N-ビニールインダゾール、N-ビニールテトラゾール、2-ビニールピリジン、4-ビニールピリジン、2-メチル-5-ビニールピリジン、2-ビニールキノリン、4-ビニールキノリン、2-ビニールピラジン、2-ビニールオキサゾール、2-ビニールベンゾオキサゾールからなる群から選択された1以上であり、前記(メタ)アクリルアミドモノマーは、N-メチルアクリルアミド、N-オクチルアクリルアミド、N-フェニルメタアクリルアミド、N-シクロヘキシルアクリルアミド、N-フェニルエチルアクリルアミド、N-p-メトキシフェニルアクリルアミド、アクリルアミド、N、N-ジメチルアクリルアミド、N、N-ジブチルアクリルアミド、N-メチル、N-フェニルアクリルアミドからなる群から選択された1以上であり、前記N-ビニール置換された環状のアミドモノマーは、N-ビニールピロリドン、N-ビニールピペリドン、N-ビニールオキサゾリドンからなる群から選択された1以上であり、前記窒素ラジカル含有芳香族置換されたエチレンモノマーは、ジメチルアミノスチレン、ジエチルアミノスチレン、ジエチルアミノメチルスチレン、ジオクチルアミノスチレンからなる群から選択された1以上であり、前記窒素含有ビニールエーテルモノマーは、ビニール-N-エチル-N-フェニルアミノエチルエーテル、ビニール-N-ブチル-N-フェニルアミノエチルエーテル、トリエタノールアミンジビニールエーテル、ビニールジフェニルアミノエチルエーテル、ビニールピロリジルアミノエーテル、ビニール-β-モルホリノエチルエーテル、N-ビニールヒドロキシエチルベンズアミド、m-アミノフェニルビニールエーテルからなる群から選択された1以上である、ことを特徴とする請求項21に記載の液体インキの製造方法。

【請求項23】 前記(b-2)段階で得られた分散液は、電荷ディレクタをさらに含む、ことを特徴とする請求項19に記載の液体インキの製造方法。

【請求項24】 前記(a-2)段階での溶媒のカウリーブタノール数値が30以上である、ことを特徴とする請求項19に記載の液体インキの製造方法。

【請求項25】 前記(d-2)段階でのキャリア液体のカウリーブタノール数値が30未満である、ことを特徴とする請求項19に記載の液体インキの製造方法。

【請求項26】 前記着色剤がカーボンブラック颜料である、ことを特徴とする請求項19に記載の液体インキの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、少なくとも一つの窒素含有重合性モノマーから誘導されるユニットを含むポリマーで表面処理された着色剤粒子を含有している液体インキ及びその製造方法に係り、より詳細には、インキ転写工程、イオノグラフ、エレクトログラフ、電子写

真カラープリンティング及びブルーフィング工程を含む全てのイメージ形成工程に使用され改善された電荷形成能力、減少した伝導度変動性、改善された分散安定性を有する液体インキ及びその製造方法に関する。

【0002】

【従来の技術】液体インキは、例えば、オフセット、バブルジェット(登録商標)、インクジェット、彫刻凹版印刷(intaglio)、輪転グラビア印刷(rotogravure)、エレクトログラフイー及び電子写真プリンティングなどのイメージ形成及び印刷工程で広く使用される。かかる液体インキは、最終のインキ組成物が実質的に相異するとしても、液体インキ用顔料分散液は各工程では大部分同一である。例えば、せん断変形条件及び高電圧電界下で使用されない顔料分散液の安定性は、液体インキの最終的な用途に無関係に重要に考慮しなければならない。

【0003】このように、安定性が改善された顔料分散液の開発により、インキ組成をより自由に構成でき、これを利用して印刷工程の効率を向上させて廃棄物量を低減する研究が継続的に行われている。

【0004】なお、液体インキは、写真複写器、レーザープリンタ、ファクシミリなどの装置を含む電子写真分野における、液体トナー又は現像液をいう。

【0005】電子写真工程は、一般に帯電された光導電体をイメージパターン方向に沿って光を照射して露光することにより、帯電された光導電体上に静電氣的イメージ潜像を形成する段階、光導電体を液体現像液と接触してイメージを現像する段階及び、最後にイメージを受像体に転写する段階を含む。最後の転写段階は、中間輸送メンバを介して直接的に又は非間接的に形成する。現像されたイメージは、一般に、熱及び/又は圧力を受けて受像体に永久に溶解される。

【0006】液体トナーは、一般に着色剤(例えば、顔料又は染料)及びポリマーバインダーからなるトナー粒子として知られている帯電粒子の分散液用キャリアの役割をする絶縁性液体を含む。電荷ディレクタは、トナー粒子上の電荷の極性及び大きさを調節する目的で付加する液体現像液成分を含むこともある。

【0007】液体トナーは2種類に分けられる。便宜上、これは通常的な液体トナー及びオルガノゾルトナーに分けられ、これらのうちオルガノゾルトナーが安定性に優れるので電子写真分野においてはより好ましい。

【0008】安定したオルガノゾルトはポリマーバインダーのコロイド粒子(直径:0.1~1μm)を含む。上記粒子は一般に低誘電性炭化水素溶媒で非水溶性分散重合によって合成される。これらオルガノゾルト粒子は物理的に吸着されたり、あるいは化学的にグラフトされた溶解性ポリマーの使用のために凝集されずに立体的に安定している。最も一般的な非水溶性分散重合方法は、炭化水素媒質に溶解されるエチレン不飽和モノマー(例えば

アクリル酸又はメタクリル酸モノマー)のうち1以上を事前成形両親媒性ポリマーの存在下での重合時に実施するフリーラジカル重合である。事前成形両親媒性ポリマーは安定剤であって、これは二つの独特のユニットより構成される。第1ユニットは炭化水素媒質に本質的に不溶であり、第2ユニットは炭化水素媒質に自由に溶解される。

【0009】オルガノゾル粒子を製造するための重合反応の実施によってモノマーが少しずつ転換して臨界分子量に到達すれば、ポリマーはその溶解度の限界を超えて溶液から沈殿形態に分離されて“コア”粒子を形成する。両親媒性ポリマーはコアに吸着されたり、共有結合を形成しており、これによってコアは成長して離散粒子を形成する。モノマーがなくなるまで粒子は成長し続け、コアに付着された両親媒性ポリマー“シェル”は成長コア粒子が凝集せずに立体的に安定化できるようにする。このように形成された非水溶性コロイド分散液(オルガノゾル)は数平均直径が0.1~0.5 μ m範囲のコア/シェルポリマー粒子を含む。

【0010】その後、上記オルガノゾルは着色剤顔料及び電荷ディレクタを単純導入したり又は混合し、高せん断均質化、ボールミリング、磨砕器ミリング、高エネルギービード(サンド)ミリング又は他の粒子大きさの減少工程又は当該技術分野で分散液形成時に粒子大きさを縮めるのに効果的である公知の混合手段による処理過程を経ることによって液体トナーを作ることができる。

【0011】ミリング時に分散液に機械的エネルギーを加えれば顔料凝集体を一次粒子(直径0.05~1.0 μ m)に作り、オルガノゾルを新しく形成された顔料表面に付着できるように破片に粉碎する役割をし、立体的に安定化した顔料粒子が凝集しないようにする。

【0012】結果的に、0.1~2.0 μ mの数平均直径を有する粒子を含んで立体的に安定化した帯電された非水溶性顔料分散液が得られ、この分散液でトナー粒子は数平均又は重量平均粒子直径が0.1~0.5 μ mである。このように、立体的に安定化した分散液は高解像度プリントに適している。

【0013】液体インキの帯電は、顔料によって非常に異なる。いわゆる“電荷調節剤”と知られている電荷ディレクタは、インキ伝導度値を許容値に調節するのに必要であり、これらの含量は着色剤顔料によって全く異なり、公知の電荷ディレクタ設計原理によってインキで設計される。相異なる着色剤顔料を含むインキは、高い電界で露光させるなどの印刷条件下で非常に異なるように作用する。着色剤顔料の相異なる帯電特性に基づいた変化は好ましくない。また、着色剤顔料のロット間変数に関して注意しなければならないが、着色剤顔料のロット間変数はインキの性質で好ましくない変化を起こすからである。したがって、着色剤顔料のタイプ又はロットに無関係に、伝導度及び電氣的特性を有するインキを有す

ることが好ましい。

【0014】また、電荷ディレクタ含量が少ないインキ、特に、現在インキ組成物で電荷ディレクタの含量が小さなブラックインキを使用すれば、印刷された光学密度を低減し、テーリング、ウォッシュオフ及びスラッジなどのオーバトーンの問題点(イメージ形成工程で副作用であると広く認識されている問題点)を低減することができる。電荷ディレクタ含量を低減しても効果的なイメージ形成のためにインキの電荷形成能力を向上させる努力、即ち、伝導度に優れたインキを製造するための努力は、電荷形成能力を向上させるのに効果がないか、又は高いフリーフェーズ伝導度などの好ましくない結果を招く。これは、トナー伝導度下のセクションで定義され、液体電子写真分野で公知の特性である。

【0015】近年、大部分の有用な電荷ディレクタは電子写真液体インキ用に適した低誘電率溶媒で制限された溶解度特性を有する。その結果、電荷ディレクタは、液体から分散された粒子又は液体インキのバインダー下で分散されたように凝集される。結果的に、着色剤顔料及び電荷ディレクタ間の直接的な物理的接触又は相互作用が殆どなく、静電的に推進された転写工程下でインキ転写が非効率的に行われる。

【0016】液体インキの分散安定性及び電荷特性を改善するための技術が下記文献に開示されている。

【0017】米国特許公報第4,665,011号には、分散された顔料と、窒素含有芳香族ビニール化合物及び無窒素芳香族ビニール化合物を含む第1ブロック、重合性C₄-C₆ジエンを含む第2ブロックを有するブロックコポリマーを含む液体インキが開示されている。これら液体インキは優れた分散安定性及び電荷安定性を有すると報告されている。

【0018】米国特許公報第5,009,980号によれば、非極性液体キャリアで実質的に不溶性又は混合されない芳香族窒素含有化合物を帯電補助剤の熱可塑性バインダーに分散させ、改善されたイメージ品質を有する液体インキを形成する。

【0019】米国特許公報第4,061,582号によれば、ポリビニールアセテートが結合剤として使用され、着色剤顔料粒子の表面にコーティングされる。処理された顔料粒子は最小限のミリング過程を経て改善された親油性を有する安定した液体インキが作製される。

【0020】

【発明が解決しようとする課題】しかしながら、上記文献には、窒素含有ポリマーを表面処理された着色剤顔料に使用する内容については特に開示されていない。

【0021】したがって、本発明の第1の目的は、窒素含有ポリマーで表面処理された着色剤を含むことにより帯電性が向上し、少量の電荷調節添加剤を使用しても伝導度特性に優れた液体インキを提供することにある。

【0022】また、本発明の第2の目的は、上記液体イ

ンキの製造方法を提供することにある。

【0023】

【課題を解決するための手段】上記課題を解決するため、本発明の第1の観点においては、キャリア液体と、オルガノゾルと、少なくとも一つの窒素含有重合性モノマーから誘導されるユニットを含むポリマーで表面処理された着色剤を含むことを特徴とする液体インキが提供される。

【0024】また、上記課題を解決するため、本発明の第2の観点においては、(a-1)少なくとも一つの窒素含有重合性モノマーから誘導されるユニットを含むポリマーを溶媒に溶解してポリマー溶液を形成する段階と、

(b-1)着色剤粒子を上記ポリマー溶液に分散して着色剤分散液を形成する段階と、(c-1)上記着色剤分散液から少なくとも若干の溶媒を除去して処理された着色剤粒子を形成する段階と、(d-1)上記処理された着色剤をキャリア液体含有オルガノゾルに分散させる段階とを含むことを特徴とする液体インキの製造方法が提供される。

【0025】また、上記課題を解決するため、本発明の第2の観点においては、(a-2)少なくとも一つの窒素含有重合性モノマーから誘導されるユニットを含むポリマーを溶媒に溶解してポリマー溶液を形成する段階と、(b-2)着色剤粒子を上記ポリマー溶液に分散して着色剤分散液を形成する段階と、(c-2)上記着色剤分散液から処理された着色剤粒子を沈積させる段階と、(d-2)上記処理された着色剤粒子をキャリア液体含有オルガノゾルに分散させる段階とを含むことを特徴とする液体インキの製造方法が提供される。

【0026】また、上記液体インキ及びこの製造方法において、上記窒素含有重合性モノマーの窒素は、アミド(amide)、アミド(amido)、アミノ及びアミングループからなる群から選択されたグループに存在することが好ましい。

【0027】そして、上記窒素含有重合性モノマーは、脂肪族アミノラジカルを有するメタクリレート又はアクリレート、窒素含有ヘテロ環ビニールモノマー、N-ビニール置換された環状のアミドモノマー、窒素ラジカル含有芳香族置換されたエチレンモノマー及び窒素含有ビニールエーテルモノマーからなる群から選択された1以上であることが好ましい。

【0028】このとき、上記脂肪族アミノラジカルを有するメタクリレート又はアクリレートは、N、N-ジメチルアミノエチル(メタ)アクリレート、N、N-ジエチルアミノエチル(メタ)アクリレート、N、N-ジブチルアミノエチル(メタ)アクリレート、N、N-ヒドロキシエチルアミノ(メタ)アクリレート、N-ベンジル-N-エチルアミノ(メタ)アクリレート、N、N-ジベンジルアミノエチル(メタ)アクリレート及びN-オクチル、N、N-ジヘキシルアミノエチル(メタ)

アクリレートからなる群から選択された1以上であり、上記窒素含有ヘテロ環ビニールモノマーは、N-ビニールイミダゾール、N-ビニールインダゾール、N-ビニールテトラゾール、2-ビニールピリジン、4-ビニールピリジン、2-メチル-5-ビニールピリジン、2-ビニールキノリン、4-ビニールキノリン、2-ビニールピラジン、2-ビニールオキサゾール、2-ビニールベンゾオキサゾールからなる群から選択された1以上であり、上記N-ビニール置換された環状のアミドモノマーは、N-ビニールピロリドン、N-ビニールピペリドン、N-ビニールオキサゾリドンからなる群から選択された1以上であり、上記窒素ラジカル含有芳香族置換されたエチレンモノマーは、ジメチルアミノスチレン、ジエチルアミノスチレン、ジエチルアミノメチルスチレン、ジオクチルアミノスチレンからなる群から選択された1以上であり、上記窒素含有ビニールエーテルモノマーは、ビニール-N-エチル-N-フェニルアミノエチルエーテル、ビニール-N-ブチル-N-フェニルアミノエチルエーテル、トリエタノールアミンジビニールエーテル、ビニールジフェニルアミノエチルエーテル、ビニールピロリジルアミノエーテル、ビニール-β-モルホリノエチルエーテル、N-ビニールヒドロキシエチルベンズアミド、m-アミノフェニルビニールエーテルからなる群から選択された1以上である。

【0029】上記(b-1)及び(b-2)段階から得られた分散液は電荷ディレクタをさらに含む。上記電荷ディレクタが多価金属イオン及びカウンタイオンである有機陰イオンより構成された金属塩であって、上記多価金属イオンはBa(II)、Ca(II)、Mn(II)、Zn(II)、Zr(IV)、Cu(II)、Al(III)、Cr(III)、Fe(II)、Fe(III)、Sb(III)、Bi(III)、Co(II)、La(III)、Pb(II)、Mg(II)、Mo(III)、Ni(II)、Ag(I)、Sr(II)、Sn(IV)、V(V)、Y(III)、Ti(IV)からなる群から選択された1以上であり、上記有機陰イオンは、脂肪族カルボン酸及び芳香族カルボン酸のうちいずれか一つから誘導されるカルボキシレート又は脂肪族スルホン酸及び芳香族スルホン酸から誘導されるスルホン酸塩からなる群から選択された1以上である。

【0030】上記(a-1)及び(a-2)段階での溶媒のカウリーブタノール数値が30以上、特に30以上150であり、上記(d-1)及び(d-2)段階でのキャリア液体のカウリーブタノール数値が30未満、特に20から30未満であることが好ましい。

【0031】また、液体インキにおいて、上記着色剤は、特にカーボンブラック顔料であることが好ましい。

【0032】

【発明の実施の形態】以下、本発明の好適な実施の形態

について、詳細に説明する。

【0033】(第1の実施の形態)本実施形態にかかる着色剤の表面処理過程は、着色剤、特に顔料の存在下で窒素含有ポリマーを沈積(沈殿物をコーティング)させたり(即ち、窒素含有ポリマー沈殿物を形成して顔料表面にコーティングしたり)、又は着色剤顔料を窒素含有ポリマー溶液で処理した後、その結果物を乾燥させる段階より構成される。

【0034】表面処理された着色剤顔料を使用すれば、帯電程度がさらに向上し、少量の電荷調節添加剤を使用しても許容可能な伝導度値を有する液体インキ及び、帯電特性においてロット及び製造者などの変数の影響が低減された顔料が得られる。

【0035】本実施形態にかかる液体インキ組成物は、キャリア液体、着色剤顔料及びオルガノソルを含む。かかる液体インキ組成物において、着色剤(特に顔料)は、キャリア液体の混合物に分散されたりする。

【0036】本実施形態にかかるインキ組成物は、凝集及び沈降されずにフィルムが迅速に形成されて(敏速な自己工程能力が有る)、特に電子写真法、イオノグラフ又は静電的イメージ形成及び他の通常の印刷工程で有用である。

【0037】上記インキ組成物において、キャリア液体は、当該技術分野で公知の色々な物質のうちで選択され、特にカウリープタノール(KB)数値が30未満(特に20以上30未満)のものをすることが好ましい。もし、キャリア液体のKB数値が上記範囲を外れる場合には、グラフト安定剤が部分的に溶解可能な領域から離れて安定剤の役割が果たせないためにインキ粒子が正常に形成されず、インキ粒子の分散性及び安定性が悪くなるので好ましくない。

【0038】KB数値は、ASTMテスト法D1133-54Tによって測定されるが、この測定法は標準溶液のカウリー数値の1-ブタノール溶液での炭化水素希釈液の付加許容度を測定するものである。KB数値は標準カウリー1-ブタノール溶液20gに付加されて所定の混濁度を与えられる25℃での溶媒の体積(ml)で表す。

【0039】参考として、KB標準値について調査値を示すが、トルエンのKB数値は105であり、ヘプタン75%及びトルエン25%からなる混合物のKB数値は40である。

【0040】上記キャリア液体は、一般に親油性であって、化学的に安定して絶縁性を有する。ここで“絶縁性を有する液体”とは、低誘電定数と高い電気抵抗率を有する液体をいう。好ましくは、この絶縁性液体は誘電定数が5以下、特に1~5であり、より好ましくは誘電定数が1~3である。このとき、キャリア液体の電気抵抗率は、 $10^9 \Omega \text{ cm}$ 以上であり、好ましくは $10^{10} \Omega \text{ cm}$ 以上、特に $10^{10} \sim 10^{16} \Omega \text{ cm}$ である。

【0041】キャリア液体は、好ましくは比較的粘性が

なく、現像時に帯電粒子が動くようにし、揮発性が十分に最終的なイメージが形成された基板から好適に除去できる。しかし、キャリア液体は非揮発性を有することから、現像液からキャリア液体が蒸発することによる損失を最小化できる。また、キャリア液体は、液体電子写真工程で使用する物質又は装置、特に感光体及びその異型表面に対して化学的に不活性でなければならない。

【0042】キャリア流体の具体的な例としては、脂肪族炭化水素(n-ペンタン、ヘキサン、ヘプタン等)、脂環族炭化水素(シクロペンタン、シクロヘキサン等)、芳香族炭化水素(ベンジン、トルエン、キシレン等)、ハロゲン化された炭化水素溶媒(塩素化されたアルカン、フッ素化されたアルカン、クロロフルオロカーボン等)、シリコンオイル類及びこれら混合物を挙げられる。キャリア流体としては、特に商品名イソパーG(Isopar G)、イソパーH、イソパーK、イソパーL、イソパーM及びイソパーV(Exxon Corporation)などの分枝型パラフィン溶媒混合物であることが好ましく、最も好ましいキャリア流体としては、商品名ノルパー12、ノルパー13及びノルパー15(Exxon Corporation)などの脂肪族炭化水素溶媒混合物を挙げられる。

【0043】グラフト安定剤は、コア部分とグラフト反応を起こしてインキ粒子を安定化させる役割をする。

【0044】グラフト安定剤の組成物は、一般にグラフト安定剤のヒルデブランド溶解度変数がキャリア流体のものに近接して対等になるように選択され、安定剤がキャリア溶媒に溶解されて十分に溶媒化されるようにする。グラフト安定剤としては、キャリア液体対比ヒルデブランド溶解度変数の差が $3.0 \text{ MPa}^{1/2}$ 未満、特に 1.0 から $3.0 \text{ MPa}^{1/2}$ 未満の重合性化合物であればいずれも使用可能である。また、もし効果的なキャリア液体対比安定剤の有効ヒルデブランド溶解度変数の差が $3.0 \text{ MPa}^{1/2}$ 未満、特に 1.0 から $3.0 \text{ MPa}^{1/2}$ 未満であれば、キャリア液体対比ヒルデブランド溶解度変数の差が $3.0 \text{ MPa}^{1/2}$ 以上の重合性化合物はコポリマーグラフト安定剤の形成時に利用される。

【0045】グラフト安定剤(シェル)とキャリア液体との間のヒルデブランド溶解度変数の絶対値差は 2.0 から $2.6 \text{ MPa}^{1/2}$ であることが特に好ましい。

【0046】グラフト安定剤の形成時に有用な重合性モノマーの非制限的な例として、3,3,5-トリメチルシクロヘキシルメタクリレート、ヘキシルアクリレート、2-エチルヘキシルアクリレート、デシルアクリレート、ドデシル(ラウリル)アクリレート、オクタデシル(ステアリル)アクリレート、ビヘニルアクリレート、ヘキシルメタクリレート、2-エチルヘキシル(メタクリレート)、デシルメタクリレート、ドデシル(ラウリル)メタクリレート、オクタデシル(ステアリル)

メタクリレート、イソボルニルアクリレート、イソボルニルメタクリレートを含むC₆-C₃₀ アクリル酸及びメタクリル酸エステル及び上記溶解度変数の必須条件を満足する他のアクリレート及びメタクリレートがある。

【0047】グラフト安定剤は樹脂コア（即ち、コアにグラフトされている）に化学的に結合されていたり、又はコアに吸着されて樹脂コアの必須領域に残留する。当該技術分野の当業者に公知された多くの反応は、フリーラジカル重合時に溶解性ポリマー安定剤をオルガノソルコアにグラフトするのに効果的である。

【0048】一般のグラフティング方法は、多官能性フリーラジカルランダムグラフティングと、サイクリックエーテル、エステル、アミド又はアセタールの開環重合と、エポキシ化反応と、不飽和性末端グループを有するヒドロキシ又はアミノ鎖移動剤の反応と、エステル化反応（即ち、グリシジルメタクリレートはメタグリル酸と反応して三次アミン触媒下でのエステル反応を進行する）及び縮合反応又は重合反応を含む。

【0049】グラフト安定剤は、数平均分子量が50, 000~1, 000, 000ダルトン（Da）であることが好ましく、より好ましくは100, 000~500, 000Da、最も好ましくは100, 000~300, 000Daである。グラフト安定剤の数平均分子量が前記範囲を外れる場合には、グラフト安定剤が部分的に溶解可能な領域から離れて安定剤の役割を行えないためにインキ粒子が正常に形成されず、インキ粒子の分散性及び安定性が悪くなるので、好ましくない。

【0050】また、グラフト安定剤の多分散性は液体トナーのイメージ形成及び転写性能に影響を及ぼす。一般にグラフト安定剤の多分散性（数平均分子量に対する重量平均分子量の比率）は1.5以下、特に1~1.5、より好ましくは2~5未満、最も好ましくは2~2.5であることが好ましい。

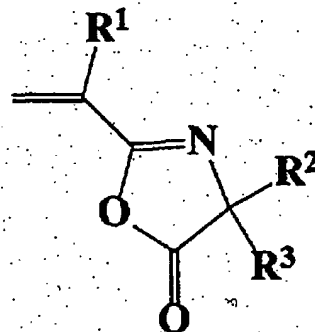
【0051】グラフティングサイトを形成するグラフティング法は、フリーラジカル重合時にグラフト安定剤にヒドロキシ基を導入し、後続の非フリーラジカル反応段階でこれらヒドロキシ基の全て又は一部をエチレン不飽和性脂肪族イソシアネート（例：メターイソプロピルジメチルベンジルイソシアネート〔TMI〕）又は2-シアナトエチルメタクリレート〔IEM〕と触媒下で反応させるものである。それから、グラフト安定剤は、後続のフリーラジカル重合段階中にグラフティングサイトの不飽和ビニルグループとエチレン不飽和コアモノマー（例：ビニルエステル、特に炭素数7未満のアクリル酸及びメタクリル酸エステル又はビニルアセレートと、スチレンなどのビニル系芳香族化合物と、アクリルニトリルと、*n*-ビニルピロリドンと、ビニルクロライド及びビニリデンクロライド）との間の反応を介して初期の不溶性アクリル酸（コ）ポリマーコアに共有結合されている。

【0052】初期の不溶性コア粒子に事前成形ポリマー安定剤をグラフティングさせる時に効果的な他の方法は当該技術の当業者に既に公知のものである。例えば、他のグラフティングプロトコルは、有機媒体でのバレット分散液重合（K. E. J. Barrett, ed., John Wiley: New York, 1975, section 3.7-3.8, pp 79-106）の文献に記載されている。ポリマー安定剤をコアにグラフティングするのに特に有用な方法は、アンカーグループを利用することである。

【0053】上記アンカーグループは、粒子のコア部と立体安定剤の溶解成分との共有輪を提供する。

【0054】上記アンカーグループを含むモノマーとしては、アルケニルアズラクトンモノマーと、2-ヒドロキシエチルメタクリレート、3-ヒドロキシプロピルメタクリレート、2-ヒドロキシエチルアクリレート、ペンタエリトリールトリアクリレート、4-ヒドロキシブチルビニルエーテル、9-オクタデセン-1-オール、シンナミルアルコール、アリルメルカプタン、メタアリルアミンなどのヒドロキシ、アミノ又はメルカプタングループを含む不飽和性求核体間の付加物及び下記構造式を有する2-アルケニル-4, 4-ジアルキルアズラクトンなどのアズラクトン類が好適である。

【0055】



【0056】上記式中、R₁はH又はC₁-C₅のアルキル基、好ましくはC₁のアルキル基であり、R₂及びR₃は各々C₁-C₈の低級アルキル基、好ましくはC₁-C₄の低級アルキル基である。

【0057】最も好ましくは、グラフティングメカニズムは、エチレン不飽和性イソシアネート（例：ジメチル-*m*-イソプロピルベンジルイソシアネート（American Cyanamid社）をグラフト安定剤前駆体（即ち、ヒドロキシエチルメタクリレート）に以前に導入したヒドロキシ基にグラフティングすることによって行われる。

【0058】コアポリマーは、安定剤モノマーとの共重合反応によってインサイチュで行われる。不溶性樹脂コアの組成物は優先的に調節されて樹脂コアが低いガラス遷移温度（T_g）を表わし、樹脂を主成分として含むイ

ンキ組成物を形成することによってコアのガラスT_g以上の温度、好ましくは23℃又はこれより高温でフィルムが迅速に形成されるように調節される（自己固定が敏速になされるようにする）。敏速な自己固定は、印刷時における欠点（例えば、汚染、トレーリング、エッジトレーリングと高速印刷時に不完全な転写を未然に防止する。コアT_gは23℃未満でのが好ましく、好ましくは10℃未満、最も好ましくは-10℃未満である。

【0059】オルガノゾルコアに適した重合性有機化合物の非制限的な例としては、メチルアクリレート、エチルアクリレート、ブチルアクリレート、メチルメタクリレート、エチルメタクリレート、ブチルメタクリレート、N、N-ジメチルアミノエチル（メタ）アクリレート、N、N-ジエチルアミノエチル（メタ）アクリレート、N、N-ジブチルアミノエチル（メタ）アクリレート、M、N-ヒドロキシエチルアミノエチル（メタ）アクリレート、N-ベンジル、N-エチルアミノエチル（メタ）アクリレート、N、N-ジベンジルアミノエチル（メタ）アクリレート、N-オクチル、N、N-ジヘキシルアミノエチル（メタ）アクリレート、N-ビニールイミダゾール（N-vinylimidazole）、N-ビニールインダゾール、N-ビニールテトラゾール、2-ビニールピリジン、4-ビニールピリジン、2-メチル-5-ビニールピリジン、2-ビニールキノリン、4-ビニールキノリン、2-ビニールピラジン、2-ビニールオキサゾール、2-ビニールベンゾオキサゾールと、N-ビニールピロリドン、N-ビニールピペリドン、N-ビニールオキサゾリドン、N-メチルアクリルアミド、N-オクチルアクリルアミド、N-フェニルメタクリルアミド、N-シクロヘキシルアクリルアミド、N-フェニルエチルアクリルアミド、N-p-メトキシフェニルアクリルアミド、アクリルアミド、N、N-ジメチルアクリルアミド、N、N-ジブチルアクリルアミド、N-メチル、N-フェニルアクリルアミドなどの（メタ）アクリルアミド類と、ピペリジンアクリレート、モルホリンアクリレート、ジメチルアミノスチレン、ジエチルアミノスチレン、ジエチルアミノメチルスチレン、ジオクチルアミノスチレン、ビニール-N-フェニルアミノエチルエーテル、ビニール-N-ブチル-N-フェニルアミノエチルエーテル、トリエタノールアミンジビニールエーテル、ビニールジフェニルアミノエチルエーテル、ビニールピロリジルアミノエーテル、ビニール-β-モルホリノエチルエーテル、N-ビニールヒドロキシエチルベンズアミド、m-アミノフェニルビニールエーテル及び他のアクリレート系及びメタクリレート、最も好ましくはメチルメタクリレート、エチルアクリレート、ジメチルアミノエチルメタクリレートなどのモノマーがある。

【0060】他のポリマーは単独で、又は上記物質と共に使用され得るが、これらポリマーの具体的な例として

は、メラミン及びメラミンホルムアルデヒド樹脂、フェノールホルムアルデヒド樹脂、エポキシ樹脂、ポリエステル樹脂、スチレン及びスチレン/アクリル酸コポリマー、ビニールアセテート及びビニールアセテート/アクリル酸コポリマー、アクリル酸及びメタクリル酸エステル、セルロースアセテート及びセルロースアセテート-ブチレートコポリマー及びポリ（ビニールブチラル）コポリマーがある。

【0061】樹脂コア及び安定剤シェルの最適重量比は、1:1から15:1であり、好ましくは2:1~10:1であり、最も好ましくは4:1~8:1である。コア/シェル比率が上記範囲を外れる場合には好ましくない効果が得られる。例えば、コア/シェル比率が15を超過すれば、オルガノゾルが凝集されずに立体的に安定化させるためのグラフト安定剤が不十分である。一方、コア/シェル比率が1未満であれば重合反応の推進力が不十分であるので、シェルが安定したオルガノゾル分散液ではない別の微粒子相が形成されたコポリマー溶液が形成される。

【0062】オルガノゾルでの粒子の大きさは、液体インキのイメージ形成過程、乾燥過程及び転写過程に影響を及ぼす。好ましくは、オルガノゾルの一次粒子の大きさ（動的光散乱法によって決定される）は、0.05~5.0μmであり、より好ましくは、0.15~1μmであり、最も好ましくは0.20~0.50μmである。

【0063】上記オルガノゾルを利用した液体インキは、熱可塑性オルガノゾル樹脂に含まれている着色剤を含む。

【0064】上記着色剤としては、当該技術分野で公知の着色剤であればいずれも有用であり、染料、ステイン、顔料などの物質を含む。

【0065】ポリマー樹脂に導入する好ましい着色剤及び顔料は、普通キャリア液体に対して不溶性及び無反応性を有し、潜像静電的イメージを可視化させるのに有用で効果的である。このような着色剤の非制限的な例として、フタロシアニンブルー（C. I. Pigment Blue 15:1, 15:2, 15:3及び15:4）、モノアリリドイエロー（C. I. Pigment イエロー 1, 3, 65, 73及び74）、ジアリリドイエロー（C. I. Pigment イエロー 2, 13, 14, 17及び83）、アリルアミド（Hansa）イエロー（C. I. Pigment イエロー 10, 97, 105及び111）、アゾレッド（C. I. Pigment Red 3, 17, 22, 23, 38, 48:1, 48:2, 52:1, 81及び179）、キナクリドンマゼンタ（C. I. Pigment Red 122, 202及び209）、微分化されたカーボン（Cabot Monarch 120, Cabot Regal 300R, Cabot Rega

1 350R, Vulcan X72)などのブラック顔料などがある。

【0066】トナー粒子で樹脂及び着色剤の最適重量比は1:1~20:1であり、好ましくは3:1~10:1であり、最も好ましくは5:1~8:1である。キャリア流体での総分散物質の含量は一般に総液体現像液組成物を基準として0.5~70重量%であり、好ましくは1~25重量%であり、最も好ましくは2~12重量%である。

【0067】着色剤顔料は、窒素含有ポリマー又はコポリマーを利用して表面処理すれば、電荷形成能力を改善させ、帯電変化を低減し得る。

【0068】窒素含有ポリマー又はコポリマーとしては、N,N-ジメチルアミノエチル(メタ)アクリレート, N,N-ジエチルアミノエチル(メタ)アクリレート, N,N-ジブチルアミノエチル(メタ)アクリレート, N,N-ヒドロキシエチルアミノ(メタ)アクリレート, N-ベンジル-N-エチルアミノ(メタ)アクリレート, N,N-ジベンジルアミノエチル(メタ)アクリレート, N-オクチル, N,N-ジヘキシルアミノエチル(メタ)アクリレートなどの脂肪族アミノラジカルを有する(メタ)アクリレート系と、N-ビニールイミダゾール, N-ビニールインダゾール, N-ビニールテトラゾール, 2-ビニールピリジン, 4-ビニールピリジン, 2-メチル-5-ビニールピリジン, 2-ビニールキノリン, 4-ビニールキノリン, 2-ビニールピラジン, 2-ビニールオキサゾール, 2-ビニールベンゾオキサゾールなどの窒素含有ヘテロ環ビニールモノマーと、N-ビニールピロリドン, N-ビニールピペリドン, N-ビニールオキサゾリドンなどのN-ビニール置換された環状のアミドモノマー; N-メチルアクリルアミド, N-オクチルアクリルアミド, N-フェニルメタクリルアミド, N-シクロヘキシルアクリルアミド, N-フェニルエチルアクリルアミド, N-p-メトキシフェニルアクリルアミド, アクリルアミド, N,N-ジメチルアクリルアミド, N,N-ジブチルアクリルアミド, N-メチル, N-フェニルアクリルアミド, ピペリジンアクリレート, モルホリンアクリレートなどの(メタ)アクリレート; ジメチルアミノスチレン, ジエチルアミノスチレン, ジエチルアミノメチルスチレン, ジオクチルアミノスチレンなどの窒素ラジカルを含む芳香族置換されたエチレンモノマー; ビニール-N-エチル-N-フェニルアミノエチルエーテル, ビニール-N-ブチル-N-フェニルアミノエチルエーテル, トリエタノールアミンジビニールエーテル, ビニールジフェニルアミノエチルエーテル, ビニールピロリジルアミノエーテル, ビニール-ベーター-モルホリノエチルエーテル, N-ビニールヒドロキシエチルベンズアミド, m-アミノフェニルビニールエーテルなどの窒素含有ビニールエーテルモノマーからなる群から選択された窒素含有重合性

有機化合物を挙げられる。

【0069】上記ポリマーは窒素原子を含むポリマーで重合ユニットのモル基準として少なくとも1%, 少なくとも2%, 少なくとも5%, 少なくとも8%, 少なくとも10%又は少なくとも15%の窒素含有重合性有機化合物を含まなければならない。窒素原子はアミド(amide), アミド(amido), アミノ又はアミン基の一部であることが好ましく、ニトロ又はシアノ置換基の一部であることは好ましくない。

【0070】着色剤顔料の表面処理は、当該技術分野で粒子の表面処理法として公知の一般的な方法によって実施できる。このような表面処理方法の非制限的な例として、溶液コーティング及び乾燥法、粉末コーティング法、顔料表面上に沈積させる方法、窒素含有ポリマー又はコポリマー存在下で顔料のミリング又は混練法、イオン浸透法及びフラッシュ処理法がある。

【0071】溶液コーティング法は、窒素含有ポリマー又はコポリマーをカウリープタノール数値が30以上、特に30~150の極性溶媒に溶解することによって行われる。窒素含有ポリマー又はコポリマー用溶媒の例としては、テトラヒドロフラン、アセトン、メチルエチルケトン、アルコール、水、メタノールなどがある。それから着色剤顔料を付加し、高せん断混合、高せん断均質化、ボールミリング、磨砕器ミリング、高エネルギービード(サンド)ミリング、又は当該技術分野において分散液での粒子大きさの減少に有効である公知の他の手段によって分散される。ミリング時に分散液に機械的エネルギーを加えれば着色剤顔料凝集体をより小さな粒子大きさに粉砕できる。

【0072】その後、オープン、真空オープン、蒸発、蒸留、スプレー乾燥器、マイクロエーブオープン、赤外線蒸発システムなどの当該技術分野における公知の乾燥法により着色剤顔料分散液から溶媒を除去することで処理された着色剤顔料粒子が形成される。

【0073】顔料表面上に沈積させる方法は、窒素含有ポリマー又はコポリマーをカウリープタノール数値が30以上、特に30~150の極性溶媒で溶解させた後、着色剤顔料を付加し、これを高せん断混合、高せん断均質化、ボールミリング、磨砕器ミリング、高エネルギービード(サンド)ミリング又は当該技術分野において分散液での粒子大きさの減少に効果的である公知の他の手段によって分散される。それから、非溶媒を付加して着色剤顔料の表面に窒素含有ポリマー又はコポリマーの沈殿物をコーティングする。

【0074】非溶媒は、窒素含有ポリマーが余り溶解されない液体であればいずれも使用できる。非溶媒は極性溶媒及び窒素含有ポリマー又はコポリマーによって選択される。

【0075】フラッシュ処理法は、水性顔料分散液を各顔料粒子表面をカバーしている水が樹脂溶液に置換さ

れた状態の樹脂溶液と混練又は混合される。このフラッシュ処理された顔料試料は乾燥されたり又は分散液として使用可能である。本実施形態にかかる上記樹脂は窒素含有ポリマー又はコポリマーである。

【0076】上記着色剤顔料の表面処理方法を参照して、本実施形態にかかる液体インキの代表的な2つの製造方法を調べれば次の通りである。

【0077】第1の製造方法は、着色剤、特に顔料の表面を上記溶液コーティング法によって処理した場合についてのものである。

【0078】まず、少なくとも一つの窒素含有重合性モノマーから誘導されるユニットを含むポリマーを溶媒に溶解してポリマー溶液を形成する。次いで、着色剤顔料粒子を上記ポリマー溶液に分散して着色剤顔料分散液を形成する。

【0079】その後、上記着色剤顔料分散液から少なくとも若干の溶媒を除去して処理された着色剤顔料粒子を形成し、このように表面処理された着色剤顔料粒子をキャリア液体含有オルガノゾルに分散させることによって本実施形態にかかる液体インキが完成される。

【0080】第2の製造方法は、着色剤（特に顔料）の表面処理時に上記顔料表面に少なくとも一つの窒素含有重合性モノマーから誘導されるユニットを含むポリマーを沈積させる方法によって実施したものである。

【0081】まず、少なくとも一つの窒素含有重合性モノマーから誘導されるユニットを含むポリマーを溶媒に溶解してポリマー溶液を形成し、着色剤顔料粒子を上記ポリマー溶液に分散して着色剤顔料分散液を形成する。

【0082】上記過程によって形成された着色剤顔料分散液から処理された着色剤顔料粒子を沈殿させ、上記処理された着色剤粒子をキャリア液体含有オルガノゾルに分散させることによって、本実施形態にかかる液体インキが完成される。

【0083】一方、電子写真液体トナーは電荷調節剤を液体インキに導入して作る。いわゆる“電荷ディレクタ”として知られている電荷調節剤は、トナー粒子に均一な電荷極性を提供する。

【0084】電荷ディレクタは、電荷ディレクタとトナー粒子を化学的に反応させる方法、トナー粒子に電荷ディレクタを物理的に吸着させる方法又は安定化グループ、抗酸化性グループ、電荷改質グループなどの作用基にキレート化する方法、トナー粒子に溶解性、非溶解性又は乳化性グループを導入する方法などの様々な方法によってトナー粒子に導入される。好ましい方法は、作用基を利用してグラフト安定剤を作ることである。電荷ディレクタは、トナー粒子の所定極性の電荷を与える役割を果たし、当該技術分野での電荷ディレクタであればいずれも使用可能である。例えば、電荷ディレクタは、多価金属イオン及びカウンタイオンとして有機陰イオンより構成された金属塩の形態に導入できる。

【0085】上記金属イオンとしては、Ba(II), Ca(II), Mn(II), Zn(II), Zr(IV), Cu(II), Al(III), Cr(III), Fe(II), Fe(III), Sb(III), Bi(III), Co(II), La(III), Pb(II), Mg(II), Mo(III), Ni(II), Ag(I), Sr(II), Sn(IV), V(V), Y(III), Ti(IV)などが適当であり、上記有機陰イオンとしては、脂肪族又は芳香族カルボン酸又はスルホン酸から誘導されるカルボキシレート又はスルホン酸塩、好ましくはステアリン酸、ベヘン酸、ネオデカン酸、ジイソプロピルサリシル酸、オクタン酸、アビエチン酸、ナフテン酸、ラウリン酸、タリン酸などの脂肪族脂肪酸がある。

【0086】好ましい正電荷ディレクタとしては、本実施形態において参照として米国特許3,411,936号に記載された金属カルボキシレート（石鹸）があり、これは少なくとも炭素数6-7の脂肪酸のアルカリ土金属及び重金属塩、ナフテン酸含有環脂肪族族酸、より好ましくはジルコニウム及びアルミニウムの多価金属石鹸であり、最も好ましくはオクタノンのジルコニウム石鹸（Zirconium HEX-CEM, Mooney Chemicals社）である。

【0087】トナー組成物に使用される好ましい電荷ディレクションレベルは、グラフト安定剤及びオルガノゾルの造成、オルガノゾルの分子量、オルガノゾルの粒子大きさ、グラフト安定剤のコア/シェル比率、トナー製造用顔料、オルガノゾルと顔料の比率を含む多くの因子によって異なる。また、好ましい電荷ディレクションレベルは、電子写真イメージ形成過程の本質、特に、現像ハードウェア及び感光性要素の設計によって異なる。しかし、当該技術分野の当業者であれば上記変数に基づいた電荷ディレクションのレベルを各々の用途において所望する結果を得られるように調節する。

【0088】液体トナーの伝導度は、当該技術分野で電子写真イメージでのトナーの効率性測定基準で明確に確立されている。なお、有用な伝導度範囲は $1.0 \times 10^{-11} \sim 10.0 \times 10^{-11}$ mho/cmである。

【0089】液体トナーの伝導度が高いことは、トナー粒子上に電荷が不十分に群集されたとことを意味する。このことは、電流密度と現像時に蓄積されたトナーとの関係が余り密接でないということから理解される。

【0090】一方、液体トナーの伝導度が低いことは、トナー粒子が帯電していないか、あるいは殆どないということの意味する。このことは、非常に低い現像速度を引き起こす。

【0091】各粒子の帯電が十分に行われるように、電荷ディレクタ化合物を使用することは一般に公知である。近年においては、電荷ディレクタを使用する方法において、キャリア流体での液体の帯電種に位置した不要

な電荷が数多く存在するという事実が明らかになった。このように不要な電荷は現像を非効率、不安定及び非一貫にする。

【0092】本実施形態においては、トナー粒子上に電荷を局部的に存在させ、かかる粒子から電荷が液体に移動することを実質的に防止し、他の不要な電荷成分が液体に存在しないようにする努めることによって上記問題点が実質的に大きく改善された。

【0093】要求される特性の基準として、本研究者らは液体トナーで示されるキャリア液体の伝導度と全般的な液体トナーの伝導度（完全に構成されたトナー分散液）との比率を使用する。この比率は0.6未満、特に0.01~0.6、好ましくは0.01~0.4、そして最も好ましくは0.01~0.3である。上記従来の他のトナーは0.95範囲でこれより大きい比率を有する。

【0094】ゲル液体トナーの製造時に顔料の粒子大きさを縮小するのに様々な方法が使用される。好適な方法としては、高せん断均質化、ボールミリング、磨砕器ミリング、高エネルギービード（サンド）ミリング又は当該技術分野で公知の他の手段を利用した方法が挙げられる。

【0095】電子写真法で、静電的イメージは一般に、（1）感光性要素を印加電圧で均一に帯電させる段階、（2）感光性要素の一部を放射供給源で露光及び帯電させて潜像イメージを形成する段階、（3）トナーを潜像イメージに加えて色相イメージを形成する段階及び、（4）色相イメージを1以上の段階を介して最終の受像体シート上に転写する段階を経ることによって感光性要素がコーティングされたシート、ドラム又はベルト上に形成される。他の用途では、色相イメージは加熱された圧力ローラ又は当該技術分野で公知の他の固定方法を利用して固定させることが好ましい。

【0096】トナー粒子又は感光性要素のうち一つの静電的電荷は正電荷又は負電荷であり、本実施形態における電子写真工程は、好ましくは正電荷で帯電された感光性要素上に電荷を分散させることによって行われる。

【0097】さらに、正電荷で帯電されたトナーは、液体トナー投入現像技術を使用して正電荷が分散された領域に加わる。この現像過程は、感光性要素表面の近くに位置している現像電極によって形成された均一な電界によって行われる。バイアス電圧は、初期帯電表面電圧と露光表面電圧レベルとの中間大きさで電極に印加する。

【0098】電圧は、要求される最大密度レベル及び蓄積されるバックグラウンドなしにハーフトーンドット用トーン再生スケールを得られるように調節する。

【0099】液体トナーは、電極と感光性要素との間を流れる。帯電されたトナー粒子は電界で流動的であり、感光性要素の帯電領域に付着され、非帯電のイメージが形成されない領域には付着されない。感光性要素に残留

する過量の液体トナーは、当該技術分野で公知の方法によって除去される。その後、感光性要素表面は乾燥させたり又は室温条件下で乾燥されるようにする。

【0100】液体インキの品質は2つの変数によって評価する。

（1）インキの伝導度

（2）経時的なインキの安定性

【0101】本実施形態にかかるインキは、低い電流ダイレクタレベルで伝導度に優れ、着色剤顔料を変化させる時、これによる伝導度変化が少ない。特に本実施形態にかかるインキは、液体投入現像電子写真工程で反転二重層感光体と結合され使用される場合、高解像度及び高速マルチカラーイメージを形成する。

【0102】感光性要素からイメージを受像する基板は、紙、コーティング紙、ポリマーフィルム及び初期の又はコーティングされたポリマーフィルムのように一般の受像体物質であればいずれも使用可能である。また、特別にコーティングされた、又は処理された金属又は金属で被覆された表面は、受像体として使用可能である。ポリマーフィルムは可塑化された及び配合されたポリビニールクロライド（PVC）、アクリル酸系、ポリウレタン系、ポリエチレン/アクリル酸コポリマー及びポリビニールブチラルを含む。また、Scotchcal, Scotchlite, Panaflex（商品名）などの商業的に入手可能な複合物が基板製造時に有用である。

【0103】帯電表面から形成されたイメージを最終的な受像体又は転写媒質に転写させる過程は、イメージを形成するために使用した分散粒子内に異型促進物質を導入して向上する。シリコン含有物質又はフッ素含有物質を粒子の外部（シェル）層に導入すればイメージの効果的な転写を促進させる。

【0104】マルチカラーイメージ形成過程において、トナーは特別にその順序が制限されず、誘電性要素又は感光性要素の表面に加わる。しかし、着色的な理由によって転写時に反転が起こる点を勘案して、カラーの透明度及び強度によって特別な順序でイメージを加えることが好ましい。例えば直接的なイメージ形成過程又はダブル転写過程で好ましい順序はイエロー、マゼンタ、シアン及びブラックの順である。また、単一転写工程で好ましい順序は、ブラック、シアン、マゼンタ及びイエローの順である。イエローは、一般に他のトナーからの汚染を避けるためにまずイメージを形成し、ブラックは一般にブラクトナーが照射供給源のフィルタとして作用するので最後にイメージを形成する。

【0105】液体インキを最も効率的に使用するための伝導度値は、50~1200 p i c o m h o - c m⁻¹の範囲である。本実施形態にかかる方法で製造された液体インキは、2.5%重量%の固体を含む分散液の場合、例えば100から500 p i c o m h o - c m

-1 である。

【0106】転写イメージをオーバーコーティングする過程は、選択的にイメージを物理的損傷及び／又は化学線損傷を保護するために実施する。オーバーコーティング組成物は、当該技術分野で公知であり、一般に揮発性溶媒に溶解されたり又は浮遊されたポリマーフィルム形成用ポリマーを含む。紫外線光吸収剤は、選択的に上記コーティング組成物に付加され得る。また、イメージ保護層をイメージが形成された表面にラミネーションする方法は当該技術分野で公知のものであって、本実施形態においては、かかる方法が使用される。

【0107】以下、本発明にかかる実施例を説明する。なお、本発明は、かかる実施例に限定されるものではない。

【0108】

【実施例】化学略語及び化学的出処の用語解説

下記原料は、本実施例のポリマー製造方法に使用されたものである。

【0109】本実施例で使用された触媒は、アゾビスイソブチロニトリル (AIBN, DuPont Chemical 社から入手した商品名 VAZO-64) 及びジブチルチンジラウレート (Dibutyl Tin Dilaurate) (DBTDL, Aldrich Chemical Co.) である。モノマーは特別に言及されていない限り、Scientific Polymer Product, Inc. から入手可能である。

【0110】本実施例のモノマーは下記略語で表示される。

【0111】ジメチル-m-イソプロペニルベンジルイソシアネート (TMI, CYTEC Industries 社)；エチルアセテート (EA)；2-エチルヘキシルメタクリレート (EHMA)；2-ヒドロキシエチルメタクリレート (HEMA)；及びメチルメタクリレート (MMA)

【0112】分析テスト方法

下記テスト方法は、本実施形態でのポリマー及びインキの特性を評価するために使用される。

【0113】グラフト安定剤、オルガノゾル及び液体トナーでの固体含量

グラフト安定剤溶液、オルガノゾル及びインキ分散液での固体含量は、精密分析秤 (Mettler Instruments Inc.) 付ハロゲンランプ乾燥オープンを使用して重量分析を実施した。約 2 g の試料で試料ドライダウン法を使用して固体含量を各々測定した。

【0114】グラフト安定剤分子量

グラフト安定剤の色々な特性は、分子量及び分子量分散性を含む安定剤の性能に重要である。グラフト安定剤分子量は一般に重量平均分子量 (M_w) で表示され、分子量分散性は重量平均分子量と数平均分子量との比

(M_w/M_n) で表示される。グラフト安定剤の分子量変数はゲル透過クロマトグラフィー (GPC) で決定されるが、このときキャリア溶媒としてはテトラヒドロフランを使用する。絶対 M_w はドーン DSP-F 光散乱検出器 (Dawn DSP-Flight scattering detector) (Wyatt Technology Corp.) で決定され、多分散性はオプチラブ (Optilab) 903 示差屈折計検出器を利用して M_n 測定分と M_w 測定値の割合で評価した。

【0115】液体トナー特性 液体トナーの特性を評価するためには、トナーの物理的及び化学的特性を測定し、LEP イメージ形成メカニズムでトナーを開発することによって得られるイメージ品質の直接的な評価が要求される。

【0116】測定されたトナー特性は大きさ関連特性 (粒子大きさ)、帯電関連特性 (バルク及びフリーフェーズ伝導度、動的移動度及びゼータポテンシャル) に大別できる。

【0117】粒子大きさ

トナー粒子大きさの分布は、ホリバ LA-900 レーザ回折粒子大きさの分析器 (Horiba LA-900 laser diffraction particle size analyzer) (Horiba Instruments, Inc.) を使用して測定した。トナー試料は約 1/500 体積比で希釈され、測定前に 150 W 及び 20 kHz で 1 分間超音波処理された。トナー粒子大きさはインキ粒子の基礎 (一次) 粒子大きさの指示者の役割を行うように数平均ベースで表現される。

【0118】トナー伝導度

液体トナー伝導度 (バルク伝導度, k_b) はサイエンティフィカモデル 6277 伝導度測定装置 (Scientifica model 6277 conductivity meter) (Scientifica Instruments, Inc.) を使用して約 18 Hz で測定された。また、トナー粒子なしにフリー (分散剤) 相伝導度 (k_f) も測定された。トナー粒子はジョアン (Joan) MR1822 遠心分離器 (Winchester, VA) で 6,000 rpm (6,110 相対遠心力)、5℃で 1~2 時間遠心分離させることによって液体環境から分離させた。

【0119】浮遊液体は、用心深く移動させ、この液体の伝導度はサイエンティフィカモデル 6277 伝導度測定装置を使用して測定した。バルクトナー伝導度に対するフリーフェーズ伝導度パーセントは 100% (k_f/k_b) で測定された。

【0120】粒子移動度

トナー粒子電気泳動移動度 (動的移動度) は、マテック MBS-8000 動電超音波振幅分析装置 (Matec MBS-8000 Electrokinetics

Sonic Amplitude Analyzer; Matec Applied Sciences, Inc.) を使用し測定した。微細電気移動に基づいた動電学測定とは異なり、MBS-8000分析装置は移動度値を得るためのトナー試料を希釈する必要がないという利点がある。したがって、印刷時に実際に好ましい固体濃度でトナー粒子の動的移動度を測定できる。

【0121】MBS-8000分析装置は、高周波数(1.2MHz)交流(AC)電界での帯電粒子の反応を測定する。高周波数AC電界では、帯電トナー粒子と周囲の分散媒質(カウンティオン含有)との間の相対的な移動によって印加電界の同じ周波数で超音波が生じる。1.2MHzでの超音波の振幅は圧電性石英変換器を利用して測定可能である。この動電超音波振幅(ESA)は粒子の低電界AC電気移動度に正比例する。さらに、粒子ゼータポテンシャルは上記装置によって動的移動度測定値及び公知のトナー粒子大きさ、分散剤液体粘度及び液体誘電定数から計算できる。

【0122】オルガノゾル

コンデンサ及びデジタル温度調節器に連結された熱電対及び乾燥窒素供給源に連結された窒素注入口及びオーバヘッド機械的攪拌器が装着された3口の丸い底を有するフラスコ5000mlに、ノルパー12(商品名)(2561g)、EHMA(849g)、96%HEMA(26.8g)及びAIBN(8.13g)の混合物を付加した。

【0123】上記混合物を機械的に攪拌しながら反応フラスコを乾燥窒素で2l/minの流速で30分間パージした。その後、中空ガラス栓をコンデンサの開口部に挿入し、窒素流速を約0.5l/minに低下させた。次いで、反応混合物を70℃で16時間加熱し、反応時間によって生成物の転換率が定量的に進行した。

【0124】上記混合物を90℃まで加熱し、その温度で1時間維持して残留AIBNを除去し70℃に調節した。その後、反応フラスコから窒素注入口を除去し、この混合物にDBTDL13.6g及びTMI41.1gを付加した。このとき、反応混合物は、磁気的な攪拌器を利用して攪拌しながら、TMIを5分にかけて少しずつ付加した。コンデンサの開口部に挿入されている中空ガラス栓を除去し、ここに窒素注入口を連結して反応フラスコ内部を窒素ガスで約2l/minの流速で30分間パージした。中空ガラス栓をコンデンサの開口部に再挿入し、窒素流速を約0.5l/minに低下させた。

【0125】次いで、反応混合物を70℃で6時間反応させることにより、反応時間によって生成物の転換率が定量的に得られた。

【0126】その後、上記反応混合物を室温で冷却させた。生成物はTMIランダム鎖を有するEHMA-HEMAコポリマーであって、EHMA/HEMA-TMI(97/3-4.7%w/w)で表示する。

【0127】上記コポリマーは8/1のコア/シェル比を有するオルガノゾルを備えるのに使用された。

【0128】オーバヘッド機械的攪拌器、コンデンサ、デジタル温度計調節器に連結された熱電対及び乾燥窒素供給源に連結された窒素注入チューブが装着された5000mlの3首の丸底フラスコにノルパー12(商品名)(2943g)、上記コポリマー(179.5g、固体含量:26.0%)、MMA(93.3g)、EA(280g)及びAIBN(6.3g)混合物を付加した。反応混合物を機械的に攪拌しながら前記フラスコを乾燥窒素で約2l/minの流速で30分間パージした。

【0129】その後、窒素ガスの流速は、約0.5l/minの速度に調節した。

【0130】反応混合物を攪拌しながら70℃に加熱し、かかる温度で16時間維持して重合させた。その後、反応混合物を室温で冷却した。

【0131】次いで、約350gのヘプタンを冷却されたオルガノゾルに付加し、得られた混合物をドライアイス/アセトンコンデンサが装着された回転蒸発器を利用して残留モノマーを除去し、95℃で作動して真空を順次に約15mmHg程度に減圧し、凝縮液の収集速度を好適な水準に維持した。モノマーが除去されたオルガノゾルを室温で冷却して不透明な白い分散液を得た。

【0132】このオルガノゾルは、コアTg(計算値)が約-1℃のEHMA/HEMA-TMI///MMA/EA(97/3-4.7//25/75%w/w)で表示される。

【0133】DSC(示差走査熱量計)によるTg(測定値)は5.7℃であった。

【0134】上記オルガノゾルでの固体含量は、上記ハロゲンドライ法を利用して測定し、測定の結果、固体含量は20.24%であった。

【0135】液体トナー実施例

(比較例1)オルガノゾル/電荷調節添加剤/ノルパープリミックス(商品名)はZrヘキセム(Hexcem)溶液(14.20g, 6.15wt%, OMC Americas Inc.), ノルパー12(商品名)(951.8g)をオルガノゾルEHMA/HEMA-TMI///MMA/EA(1034.0g)に付加し、上記混合物を実験室用シェカを利用して約30分間振動させた。ポッタスガラスビード(Potter's Glass beads)390g、オルガノゾル/電荷調節剤/ノルパープリミックス294.9g及び未処理のモナーク120(Lot 485-732, Carbot社)で充填されたイガラシセル(Igarashi cell)0.5Lを処理された顔料の代わりに使用した。

【0136】組成物を2000rpmで90分間ミリングして顔料1g当たり電荷調節剤(CCA)25mg含

量のブラックインキを得た。

【0137】ブラックインキの粒子大きさ及び伝導度は上記方法によって測定した。

【0138】測定の結果、3wt%ブラックインキの伝導度は105 pmho/cmであり、フリーフェーズ伝導度は、1.42 pmho/cm (1.35%フリーフェーズ伝導度)であり、体積平均粒子大きさ (Horiba 910) は0.84 μmであった。粒子大きさ分布は約1.20 μmで最大値を有するモノモードを示した。このトナーを使用すれば、薄いバックグラウンド現像及び500V現像液バイアスで1.49の反射光学密度で満足できる印刷結果が得られる。

【0139】(実施例1) カーボンブラック顔料 (20.0g, Monach 120, lot 485-732, Carbot社) 及び変性アルコール (60.0g) を400mlのポリエチレンビーカー入れた。

【0140】上記混合物をポリトロン実験室用分散装置 (Model #PT10/35, Kinematica社) を使用して約3分間均質化させて粘度性ペーストを得た。ポリ (2-ビニールピリジン-コースチレン) の変性アルコール溶液 (20.0g, 2.5wt%溶液, M_w = 約220,000 (ここで、重量平均分子量が好適なベースであるが、数平均分子量を使用する。スチレン含量: 30%, Aldrich Chemical Company) をカーボンブラック分散液に付加した。

【0141】均質化過程は低粘度ブラック分散液が得られるまで実施した。2.5wt%のポリ (2-ビニールピリジン-コースチレン) 60.0gを分散液に付加し、均質化過程は、No. 5にセットした状態で約10分間実施し続けた。

【0142】顔料とポリマーの混合重量比は10:1であった。実験室用攪拌器を使用して攪拌しながらブラック分散液を脱イオン水2600gに徐々に注いだ。脱イオン水での顔料分散液をろ過紙 (Whatman #54) を介してろ過し、約150gの脱イオン水で2回洗浄した。

【0143】上記過程によって収集された顔料を50℃で20時間乾燥させ、その後、実験室用乳鉢及び乳棒を利用してポリ (2-ビニールピリジン-コースチレン) 処理されたモナーク120顔料を得た。

【0144】オルガノゾル/電荷調節剤/ノルパープリミックス (商品名) はZrヘキセム (Hexcem) 溶液 (14.20g, 6.15wt%, OMG Americas Inc.), ノルパー12 (商品名) (951.8g) をオルガノゾルEHMA/HEMA-TMI//MMA/EA (1034.0g) に付加し、上記混合物を実験室用シェーカを利用して約30分間振動させた。

【0145】0.5Lのイガラシセルにポッタスガラス

ビード390g, オルガノゾル/電荷調節剤/ノルパープリミックス (商品名) 294.9g及びポリ (2-ビニールピリジン-コースチレン) 処理されたモナーク120顔料5.65gを充填した。組成物を2000rpmで90分間ミリングして顔料1g当たり電荷調節剤 (CCA) 25mg含量のブラックインキを得た。

【0146】ブラックインキの粒子大きさ及び伝導度は、上記方法によって測定した。

【0147】測定の結果、3wt%ブラックインキの伝導度は185 pmho/cmであり、フリーフェーズ伝導度は9.71 pmho/cm (5.2%フリーフェーズ伝導度)であり、体積平均粒子大きさ (Horiba 910) は2.56 μmであった。粒子大きさの分布は、約1.25 μm及び4 μmで最大値を有するバイモード (bi-modal) (シヨルダー、トナーの約30体積%)を示した。このトナーを用いれば、500V現像液バイアスで1.44の反射光学密度で満足できる印刷結果が得られる。

【0148】上記実験結果から、ポリ (2-ビニールピリジン-コースチレン) で処理されたカーボンブラック顔料は、顔料の電荷形成能力を改善するのに効果的であって、伝導度が135 pmho以上で、かつ顔料1g当たりCCA25mg含量のインキが得られる。

【0149】(実施例2) カーボンブラック顔料 (20.0g, Monach 120, lot 485-732, Carbot社), 変性アルコール (60.0g), ポリ (2-ビニールピリジン-コブチルメタクリレート) (2.5wt%溶液約60g, プチルメタクリレート含量: 10%, Aldrich Chemical Company社) を400mlのポリエチレンビーカーに入れた。

【0150】上記反応混合物をポリトロン実験室用分散装置 (Model #PT10/35, Kinematica社) を使用して約3分間均質化させ、カーボンブラック分散液を得た。このカーボンブラック分散液にポリ (2-ビニールピリジン-コブチルメタクリレート) の変性アルコール溶液 (100.0g, 2.5wt%の変性アルコール溶液) を入れた。

【0151】上記混合物の均質化過程は、No. 5にセットした状態で約10分間実施し続けた。顔料とポリマーの混合重量比は5:1である。

【0152】次いで、反応混合物を実験室用攪拌器を使用して攪拌しながらブラック分散液を脱イオン水2200gに徐々に注いだ。脱イオン水での顔料分散液は、ろ過紙 (Whatman #54) を介してろ過し、約150gの脱イオン水で2回洗浄した。

【0153】上記過程によって収集された顔料を50℃で20時間乾燥し、その後、実験室用乳鉢及び乳棒を利用してポリ (2-ビニールピリジン-コブチルメタクリレート) 処理されたモナーク120顔料を得た。

【0154】オルガノゾル／電荷調節剤／ノルパープリミックス（商品名）はZrヘキセム（Hexcem）溶液（14.20g, 6.15wt%, OMG Americas Inc.）, ノルパー12（商品名）（951.8g）をオルガノゾルEHMA/HEMA-TMI///MMA/EA（1034.0g）に付加し、上記混合物を実験室用シェーカを利用して約30分間振動させた。

【0155】0.5Lのイガラシセルにポッタスガラスビード390g, オルガノゾル／電荷調節剤／ノルパープリミックス（商品名）294.9g及びポリ（2-ビニルピリジン-コ-ブチルメタクリレート）処理されたモナーク120顔料6.16gを充填した。

【0156】組成物を2000rpmで90分間ミリングして顔料1g当たり電荷調節剤（CCA）25mg含量のブラックインキを得た。

【0157】ブラックインキの粒子大きさ及び伝導度は上記方法によって測定した。

【0158】測定の結果、3wt%ブラックインキの伝導度は233pmho/cmであり、フリーフェーズ伝導度は11.74pmho/cm（5.0%フリーフェーズ伝導度）であり、体積平均粒子大きさ（Horiba 910）は11.0μmであった。粒子大きさの分布は約13μm（約85wt%）及び1.5μm（約15wt%）で最大値を有するバイモードを示した。

【0159】上記実験結果から、ポリ（2-ビニルピリジン-コ-ブチルメタクリレート）で処理されたカーボンブラック顔料は、トナー粒子大きさの分布を高めるのに効果的であり、また、顔料の電荷形成能力を改善させるのに効果的であって、伝導度が135pmho以上で、かつ顔料1g当たりCCA25mg含量のインキを得られる。

【0160】（実施例3）ポリ（1-ビニルピロリドン-コ-2-ジメチルアミノエチルメタクリレート）水溶液（19wt%水溶液10.0g, Mw=1,000, Aldrich Chemical Company社）を400mlのビーカーに入れ、沸騰している脱イオン水190gを付加して高温の希釈されたポリマー溶液を得た。この高温溶液をカーボンブラック顔料（20.0g, Monarch 120, lot 485-732, Carbot社）に付加し、この混合物を磁気的な実験室用攪拌器を利用して10分間攪拌した。このように得られたスラリーをろ過紙（Whatman #5）を通過してろ過させて約100mlの体積に濃縮した。このとき、スラリーのろ過過程は非常に遅く進行された。また、ろ過紙に残っている塊は、ブラックチキソトロピーゲル状塊であった。

【0161】その後、ろ過紙に残存する残留物を50℃に調節されたオープンで7日間乾燥し、乳鉢及び乳棒を使用して手で粉末化した後、ポリ（1-ビニルピロリ

ドン-2-ジメチルアミノエチルメタクリレート）処理されたカーボンブラック顔料を得た。

【0162】オルガノゾル／電荷調節剤／ノルパープリミックス（商品名）は、Zrヘキセム（Hexcem）溶液（14.20g, 6.15wt%, OMG Americas Inc.）, 商品名ノルパー12（951.8g）をオルガノゾルEHMA/HEMA-TMI///MMA/EA（1034.0g）に付加し、上記混合物を実験室用シェーカを利用して約30分間振動させた。0.5Lのイガラシセルにポッタスガラスビード390g, オルガノゾル／電荷調節剤／ノルパープリミックス（商品名）294.9g及びポリ（2-ビニルピリジン-コ-ブチルメタクリレート）処理されたモナーク120顔料5.14gを充填した。上記組成物を2000rpmで90分間ミリングして顔料1g当たり電荷調節剤（CCA）25mg含量のブラックインキを得た。

【0163】ブラックインキの粒子大きさ及び伝導度は上記方法によって測定した。

【0164】測定の結果、3wt%ブラックインキの伝導度は、167pmho/cmであり、フリーフェーズ伝導度は、7.11pmho/cm（4.3%フリーフェーズ伝導度）であり、体積平均粒子大きさ（Horiba 910）は、5.291μmであった。粒子大きさの分布は約1.3μm（トナーの約40体積%）及び8.5μm（トナーの約60体積%）でバイモードを示した。このトナーを利用すれば、500Vの現像液バイアスで1.29の反射光学密度で満足できる印刷結果が得られる。

【0165】上記実験結果から、ポリ（1-ビニルピロリドン-コ-2-ジメチルアミノエチルメタクリレート）で処理されたカーボンブラック顔料は顔料の電荷形成能力を改善させるのに効果的であって、導電率が135pmho以上で、かつ顔料1g当たり25mg CCA含量のインキを得ることができた。

【0166】（実施例4）カーボンブラック顔料（20.0g, Monarch 120, lot 485-732, Carbot社）をポリ（ビニルピロリドン-コ-ビニルアセテート）溶液（100.0g, PVP/VAE-335, 変性アルコールでの0.67wt%溶液, ISP Technologies Inc.）に付加した。

【0167】上記混合物をポリトロン実験室用分散装置で約10分間均質化させてカーボンブラック分散液を得た。このカーボンブラック分散液で顔料とポリマーの混合重量比は30:1であった。

【0168】上記ブラック分散液をアルミニウムパンに入れ、これを80℃で約20時間乾燥させた後、実験室用乳鉢及び乳棒を利用して粉末化し、ポリ（ビニルピロリドン-コ-ビニルアセテート）処理されたモナーク

ク120顔料を得た。

【0169】オルガノゾル／電荷調節剤／ノルパープリミックス（商品名）はZrヘキセム溶液（14.20g, 6.15wt%, OMG Americas Inc.）, ノルパー12（商品名）（951.8g）をオルガノゾルEHMA/HEMA-TMI//MMA/EA（1034.0g）に付加し、これら混合物を実験室用シェーカを利用して約30分間振動させた。

【0170】0.5Lのイガラシセルにポッタスガラスビード390g, オルガノゾル／電荷調節剤／ノルパープリミックス（商品名）294.9g及びポリ（ビニルピロリドン－コービニールアセテート）処理されたモナーク120顔料5.31gを充填した。上記組成物を2000rpmで90分間ミリングしてポリ（ビニルピロリドン－コービニールアセテート）のない、顔料1g当たり電荷調節剤（CCA）25mg含量のブラックインキを得た。

【0171】ブラックインキの粒子大きさ及び伝導度は、上記方法によって測定した。

【0172】測定の結果、3wt%ブラックインキの伝導度は、145pmho/cmであり、フリーフェーズ伝導度は6.77pmho/cm（4.7%フリーフェーズ伝導度）であり、体積平均粒子大きさ（Horiba 910）は1.04μmであった。粒子大きさの分布はモノモードを示した。

【0173】上記実験結果から、ポリ（ビニルピロリドン－コービニールアセテート）で処理されたカーボンブラック顔料は顔料の電荷形成能力を改善させるのに効果的であって、伝導度が135pmho以上であり、顔料1g当たりCCA25mg含量のインキを得られた。本実施例から、伝導度を改善させるために処理されたカーボンブラック顔料を使用すれば、これは上記条件下でミリングする場合、未処理のブラック顔料に比べてトナー粒子大きさを増加させないということが認識された。

【0174】（実施例5）透明なガラス瓶にトルエン210g, スチレン（Aldrich Chemical Company）72.0g, ジメチルアミノエチルメタクリレート（Aldrich Chemical Company）, 28.0g, 2,2'-アゾイソブチロニトリル（AIBN, Aldrich Chemical Company）1.35gを入れた。このように得られた溶液を窒素ガスで10分間パージし、70℃に調節された沸騰水槽（Lauder-O-meter, Atlas Electric Products 社）が装着されたタンブラ内に配置させた。

【0175】上記混合物を16時間タンブラさせつつ70℃で反応させた後、タンブラから取り出して室温で冷却させた。次いで、反応混合物にスチレン72.0g, ジメチルアミノエチルメタクリレート28.0g, AIBN 1.35gをさらに付加した後、ここに窒素を再

びパージした後、70℃で20時間タンブリングさせた。こうして得られたポリマーのトルエン溶液を約3500mlのヘプタンに注いで粘調度類似ペーストを有する不透明性粘性液体形態の沈殿物を得た。次いで、ヘプタンを沈殿ポリマーから移動させ、ポリマーを排気口を有するオープンで2日間乾燥させた。

【0176】乾燥されたガラス質ポリマーをトルエンに溶かした後、これら沈殿物形成過程を2回反復し、移動及び乾燥させてスチレン／ジメチルアミノエチルメタクリレートモル比（計算値）が8：2のポリ（スチレン－コージメチルアミノエチルメタクリレート）ガラス質固体生成物を得た。

【0177】その後、カーボンブラック顔料（20.0g, Monarch 120, lot 485-732, Cabot 社）を2.0wt%ポリ（スチレン－コージメチルアミノエチルメタクリレート）のアセトン溶液100gに入れた。

【0178】上記混合物をポリトロン実験室用分散装置を使用して約10分間均質化させブラック分散液を得た。このブラック分散液で顔料とポリマーの混合重量比は10：1であった。

【0179】上記ブラック分散液を、実験室用攪拌器で攪拌している脱イオン水2,600gに徐々に注入した後、反応混合物を30分間攪拌し続けた。脱イオン水中の顔料分散液をろ過紙（Whatman #54）を介してろ過し、約150gの脱イオン水で2回洗浄した。

【0180】上記過程によって収集された顔料を80℃で20時間乾燥させた後、実験室用乳鉢及び乳棒を使用して手で粉末化させ、ポリ（スチレン－コージメチルアミノエチルメタクリレート）処理されたモナーク120顔料を得た。

【0181】オルガノゾル／電荷調節剤／ノルパープリミックス（商品名）はZrヘキセム溶液（14.20g, 6.15wt%, OMG Americas Inc.）, ノルパー12（商品名）（951.8g）をオルガノゾルEHMA/HEMA-TMI//MMA/EA（1034.0g）に付加し、これら混合物を実験室用シェーカを利用して約30分間振動させた。

【0182】0.5Lのイガラシセルにポッタスガラスビード390g, オルガノゾル／電荷調節剤／ノルパープリミックス（商品名）294.9g及びポリ（スチレン－コージメチルアミノエチルメタクリレート）処理されたモナーク120顔料5.65gを充填した。上記組成物を2000rpmで90分間ミリングしてポリ（スチレン－コージメチルアミノエチルメタクリレート）のない、顔料1g当たり電荷調節剤（CCA）25mg含量のブラックインキを得た。

【0183】ブラックインキの粒子大きさ及び伝導度は上記方法によって測定した。

【0184】測定の結果、3wt%ブラックインキの伝

導度は、 135 pmho/cm であり、フリーフェーズ伝導度は、 5.12 pmho/cm （3.8%フリーフェーズ伝導度）であり、体積平均粒子大きさ（Horiba 910）は $0.86 \mu\text{m}$ であった。粒子大きさの分布は、モノモードを示した。

【0185】上記実験結果から、ポリ（スチレンーコージメチルアミノエチルメタクリレート）で処理されたカーボンブラック顔料は顔料の電荷形成能力を改善させるのに効果的で、伝導度が 135 pmho 以上であり、顔料1g当たりCCA25mg含量のインキを得られた。かかる実施例から、伝導度を改善させるために処理されたカーボンブラック顔料を使用すれば、上記条件下でミリングする場合に未処理のブラック顔料に比べてトナー

粒子大きさを増加させない。

【0186】以上、本発明に係る好適な実施の形態について説明したが、本発明はかかる構成に限定されない。当業者であれば、特許請求の範囲に記載された技術思想の範囲内において、各種の修正例および変更例を想定し得るものであり、それらの修正例および変更例についても本発明の技術範囲に包含されるものと了解される。

【0187】

【発明の効果】少なくとも一つの窒素含有重合性モノマーから誘導されるユニットを含むポリマーで表面処理された着色剤を含むことによって、改善された電荷形成能力と減少した伝導度変動性及び改善された分散安定性を有する液体インキを得られる。

フロントページの続き

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CLAIMS

Claim(s)

[Claim 1] Liquid ink characterized by including a carrier liquid, an organosol, and the coloring agent by which surface treatment was carried out by the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer.

[Claim 2] Said coloring agent is liquid ink according to claim 1 characterized by what is been the pigment by which surface treatment was carried out with surface coating or a surface chemical modification method.

[Claim 3] Said carrier liquid is liquid ink according to claim 1 which consists of aliphatic hydrocarbon, an alicycle group hydrocarbon, aromatic hydrocarbon, the halogenated hydrocarbon solvent, silicone oils, and these mixture, and is characterized by what the Cowley butanol numeric value is less than 30.

[Claim 4] Said liquid ink is liquid ink according to claim 1 characterized by what a charge director is further included for.

[Claim 5] While said charge director is the metal salt which consisted of organic anions which are polyvalent metal ion and counter ion Said polyvalent metal ion Ba (II), calcium (II), Mn (II), Zn (II), Zr (IV), Cu (II), aluminum (III), Cr (III) and Fe (II), Fe (III), Sb (III), Bi (III), Co (II), La (III), Pb (II), Mg (II), Mo (III) and nickel (II), Ag (I), It is, or more [it was chosen from the group which consists of Sr (II), Sn (IV), V (V), and Y (III) and Ti (IV)] one. And said organic anion Liquid ink according to claim 4 characterized by what is been the sulfonate guided from one chosen from the carboxylate or aliphatic series sulfonic acid, and aromatic series sulfonic acid which are guided from any one of aliphatic carboxylic acid and aromatic carboxylic acid.

[Claim 6] Said nitrogen is liquid ink according to claim 1 characterized by what is existed in the group chosen from the group which consists of an amide (amide), an amide (amido), amino, and an amine group.

[Claim 7] Said nitrogen content polymerization nature monomer is liquid ink according to claim 1 characterized by what is been or more [it was chosen from the group which consists of the methacrylate which has an aliphatic series amino radical or acrylate, a nitrogen content heterocycle vinyl monomer, the annular amide monomer by which N-vinyl permutation was carried out, an acrylamide (meta) monomer, an ethylene monomer by which nitrogen radical content aromatic substitution was carried out, and a nitrogen content vinyl ether monomer] one.

[Claim 8] The methacrylate or acrylate which has said aliphatic series amino radical N and N-dimethylaminoethyl (meta) acrylate, N and N-diethylaminoethyl Acrylate, N, and N-dibutyl aminoethyl (meta) acrylate, N, and N-hydroxyethylamino (meta) acrylate, N-benzyl-N-ethylamino (meta) acrylate, N, and N-dibenzyl aminoethyl (meta) acrylate (Meta) It is, or more [it was chosen from the group which consists of N-octyl, N, and N-dihexyl aminoethyl (meta) acrylate] one. And said nitrogen content heterocycle vinyl monomer N-vinyl imidazole, N-vinyl indazole, N-vinyl tetrazole, 2-vinyl pyridine, 4-vinyl pyridine, a 2-methyl-5-vinyl pyridine, 2-vinyl quinoline, 4-vinyl quinoline, 2-vinyl pyrazine, It is, or more [it was chosen from the group which consists of 2-vinyl oxazole and 2-vinyl benzoxazole] one. The aforementioned (meta) acrylamide monomer N-methylacrylamide, N-octyl acrylamide, N-phenyl meta-acrylamide, N-cyclohexyl acrylamide, N-phenylethyl acrylamide, N-p-methoxy-phenyl acrylamide, acrylamide, N, It is, or more [it was chosen from the group which consists of N-dimethyl acrylamide, N, and N-dibutyl acrylamide, N-methyl and N-phenyl acrylamide] one. Said annular amide monomer by which N-vinyl permutation was carried out N vinylpyrrolidone, N-BINIRUPI ** RIDON, It is, or more [it was chosen from the group which consists of N-vinyl oxazolidone] one. Said ethylene monomer by which nitrogen radical content aromatic substitution was carried out It is, or more [it was chosen from the group which consists of dimethylamino styrene, diethylamino styrene, diethylamino methyl styrene, and dioctylamino styrene] one. Said nitrogen content vinyl ether monomer Vinyl-N-ethyl-N-phenylamino ethyl ether, Vinyl-N-butyl-N-phenylamino ethyl ether, triethanolamine divinyl oxide, vinyl diphenylamino ethyl ether, the vinyl pyrrolidyl amino ether, vinyl-beta-morpholino ethyl ether, Liquid ink according to claim 7 characterized by what is been or more [it was chosen from the group which consists of an N-vinyl

hydroxyethyl benzamide and m-aminophenyl vinyl ether] one.

Claim 9] The weight average molecular weight of said polymer is liquid ink according to claim 1 characterized by what is been 50,000 to 150,000dalton.

Claim 10] Said coloring agent is liquid ink according to claim 1 characterized by what is been a carbon black pigment.

Claim 11] (a-1) The phase which dissolves the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer in a solvent, and forms a polymer solution, The phase which distributes a color particle in said polymer solution, and forms coloring agent dispersion liquid, (b-1) (c-1) The manufacture approach of the liquid ink characterized by including the phase which forms the color particle which removed some solvent at least and was processed from said coloring agent dispersion liquid, and the phase of making a carrier liquid content organosol distributing said (d-1) processed coloring agent.

Claim 12] The nitrogen atom in said nitrogen content polymerization nature monomer is the manufacture approach of the liquid ink according to claim 11 characterized by what is existed in the group chosen from the group which consists of an amide (amide), an amide (amido), amino, and an amine group.

Claim 13] Said nitrogen content polymerization nature monomer is the manufacture approach of the liquid ink according to claim 11 characterized by what is been or more [it was chosen from the group which consists of the methacrylate which has an aliphatic series amino radical or acrylate, a nitrogen content heterocycle vinyl monomer, the annular amide monomer by which N-vinyl permutation was carried out, an acrylamide (meta) monomer, an ethylene monomer by which nitrogen radical content aromatic substitution was carried out, and a nitrogen content vinyl ether monomer] one.

Claim 14] The methacrylate or acrylate which has said aliphatic series amino radical N and N-dimethylaminoethyl (meta) acrylate, N and N-diethylaminoethyl Acrylate, N, and N-dibutyl aminoethyl (meta) acrylate, N, and N-hydroxyethylamino (meta) acrylate, N-benzyl-N-ethylamino (meta) acrylate, N, and N-dibenzyl aminoethyl (meta) acrylate (Meta) It is, or more [it was chosen from the group which consists of N-octyl, N, and N-dihexyl aminoethyl (meta) acrylate] one. And said nitrogen content heterocycle vinyl monomer N-vinyl imidazole, N-vinyl indazole, N-vinyl tetrazole, 2-vinyl pyridine, 4-vinyl pyridine, a 2-methyl-5-vinyl pyridine, 2-vinyl quinoline, 4-vinyl quinoline, 2-vinyl pyrazine, It is, or more [it was chosen from the group which consists of 2-vinyl oxazole and 2-vinyl benzooxazole] one. The aforementioned (meta) acrylamide monomer N-methylacrylamide, N-octyl acrylamide, N-phenyl meta-acrylamide, N-cyclohexyl acrylamide, N-phenylethyl acrylamide, N-p-methoxy-phenyl acrylamide, acrylamide, N, It is, or more [it was chosen from the group which consists of N-dimethyl acrylamide, N, and N-dibutyl acrylamide, N-methyl and N-phenyl acrylamide] one. Said annular amide monomer by which N-vinyl permutation was carried out N vinylpyrrolidone, N-BINIRUPI ** RIDON, It is, or more [it was chosen from the group which consists of N-vinyl oxazolidone] one. Said ethylene monomer by which nitrogen radical content aromatic substitution was carried out It is, or more [it was chosen from the group which consists of dimethylamino styrene, diethylamino styrene, diethylamino methyl styrene, and dioctylamino styrene] one. Said nitrogen content vinyl ether monomer Vinyl-N-ethyl-N-phenylamino ethyl ether, Vinyl-N-butyl-N-phenylamino ethyl ether, triethanolamine divinyl oxide, vinyl diphenylamino ethyl ether, the vinyl pyrrolidyl amino ether, vinyl-beta-morpholino ethyl ether, The manufacture approach of the liquid ink according to claim 13 characterized by what is been or more [it was chosen from the group which consists of an N-vinyl hydroxyethyl benzamide and m-aminophenyl vinyl ether] one.

[Claim 15] The dispersion liquid obtained in the aforementioned (b-1) phase are the manufacture approach of the liquid ink according to claim 11 characterized by what a charge director is further included for.

[Claim 16] The manufacture approach of the liquid ink according to claim 11 characterized by what the Cowley butanol numeric value of the solvent in the aforementioned (a-1) phase is 30 or more.

[Claim 17] The manufacture approach of the liquid ink according to claim 11 characterized by what the Cowley butanol numeric value of the carrier liquid in the aforementioned (d-1) phase is less than 30.

[Claim 18] Said coloring agent is the manufacture approach of the liquid ink according to claim 11 characterized by what is been a carbon black pigment.

[Claim 19] (a-2) The phase which dissolves the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer in a solvent, and forms a polymer solution, The phase which distributes a color particle in said polymer solution, and forms coloring agent dispersion liquid, (b-2) (c-2) The manufacture approach of the liquid ink characterized by including the phase of carrying out the sediment of the color particle processed from said coloring agent dispersion liquid, and the phase of making a carrier liquid content organosol distributing said (d-2) processed color particle.

[Claim 20] Said nitrogen is the manufacture approach of the liquid ink according to claim 19 characterized by what is

existed in the group chosen from the group which consists of an amide (amide), an amide (amido), amino, and an imine group.

[Claim 21] Said nitrogen content polymerization nature monomer is the manufacture approach of the liquid ink according to claim 19 characterized by what is been or more [it was chosen from the group which consists of the methacrylate which has an aliphatic series amino radical or acrylate, a nitrogen content heterocycle vinyl monomer, the annular amide monomer by which N-vinyl permutation was carried out, an acrylamide (meta) monomer, an ethylene monomer by which nitrogen radical content aromatic substitution was carried out, and a nitrogen content vinyl ether monomer] one.

[Claim 22] The methacrylate or acrylate which has said aliphatic series amino radical N and N-dimethylaminoethyl (meta) acrylate, N and N-diethylaminoethyl Acrylate, N, and N-dibutyl aminoethyl (meta) acrylate, N, and N-hydroxyethylamino (meta) acrylate, N-benzyl-N-ethylamino (meta) acrylate, N, and N-dibenzyl aminoethyl (meta) acrylate (Meta) It is, or more [it was chosen from the group which consists of N-octyl, N, and N-dihexyl aminoethyl (meta) acrylate] one. And said nitrogen content heterocycle vinyl monomer N-vinyl imidazole, N-vinyl indazole, N-vinyl tetrazole, 2-vinyl pyridine, 4-vinyl pyridine, a 2-methyl-5-vinyl pyridine, 2-vinyl quinoline, 4-vinyl quinoline, 2-vinyl pyrazine, It is, or more [it was chosen from the group which consists of 2-vinyl oxazole and 2-vinyl benzoxazole] one. The aforementioned (meta) acrylamide monomer N-methylacrylamide, N-octyl acrylamide, N-phenyl meta-acrylamide, N-cyclohexyl acrylamide, N-phenylethyl acrylamide, N-p-methoxy-phenyl acrylamide, acrylamide, N, It is, or more [it was chosen from the group which consists of N-dimethyl acrylamide, N, and N-dibutyl acrylamide, N-methyl and N-phenyl acrylamide] one. Said annular amide monomer by which N-vinyl permutation was carried out N-vinylpyrrolidone, N-BINIRUPI ** RIDON, It is, or more [it was chosen from the group which consists of N-vinyl oxazolidone] one. Said ethylene monomer by which nitrogen radical content aromatic substitution was carried out It is, or more [it was chosen from the group which consists of dimethylamino styrene, diethylamino styrene, diethylamino methyl styrene, and dioctylamino styrene] one. Said nitrogen content vinyl ether monomer Vinyl-N-ethyl-N-phenylamino ethyl ether, Vinyl-N-butyl-N-phenylamino ethyl ether, triethanolamine divinyl oxide, vinyl diphenylamino ethyl ether, the vinyl pyrrolidyl amino ether, vinyl-beta-morpholino ethyl ether, The manufacture approach of the liquid ink according to claim 21 characterized by what is been or more [it was chosen from the group which consists of an N-vinyl hydroxyethyl benzamide and m-aminophenyl vinyl ether] one.

[Claim 23] The dispersion liquid obtained in the aforementioned (b-2) phase are the manufacture approach of the liquid ink according to claim 19 characterized by what a charge director is further included for.

[Claim 24] The manufacture approach of the liquid ink according to claim 19 characterized by what the Cowley butanol numeric value of the solvent in the aforementioned (a-2) phase is 30 or more.

[Claim 25] The manufacture approach of the liquid ink according to claim 19 characterized by what the Cowley butanol numeric value of the carrier liquid in the aforementioned (d-2) phase is less than 30.

[Claim 26] The manufacture approach of the liquid ink according to claim 19 characterized by what said coloring agent is a carbon black pigment.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the liquid ink containing the color particle by which surface treatment was carried out by the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer, and its manufacture approach. In a detail, more An ink imprint process, an IONO graph, an electrograph, It is related with the liquid ink which has the charge organization potency force which was used for all image formation processes including electrophotography color printing and a PURUFINGU process, and has been improved, the conductivity variability which decreased, and the improved distributed stability, and its manufacture approach.

[0002]

[Description of the Prior Art] Liquid ink is widely used by image formation and presswork, such as offset, bubble jet (trademark), an ink jet, sculpture intaglio printing (intaglio), rotogravure printing (rotogravure), electrography, and electrophotography printing. Though the last ink constituent carries out difference of this liquid ink substantially, the pigment dispersion liquid for liquid ink are mostly the same at each process. For example, the stability of the pigment dispersion liquid which are not used under shear strain conditions and high-tension electric field must be independently taken into consideration importantly for the final application of liquid ink.

[0003] Thus, research which an ink presentation can be constituted more freely, and the effectiveness of presswork is raised using this, and reduces the amount of trash by development of the pigment dispersion liquid by which stability has been improved is done continuously.

[0004] In addition, liquid ink says the liquid toner or developer in the electrophotography field containing equipments, such as a photocopy machine, a laser beam printer, and facsimile.

[0005] An electrophotography process includes the phase which forms the static electricity-image latent image on the electrified photo conductor, the phase of contacting liquid development liquid in a photo conductor, and developing an image, and the phase which imprints an image on a television object at the last by irradiating light and exposing the photo conductor generally charged along the direction of an image pattern. The last imprint phase is formed directly or in un-indirect through a medium transport member. Generally in response to heat and/or a pressure, melting of the developed image is eternally carried out to a television object.

[0006] A liquid toner contains the insulating liquid which carries out the role of the carrier for dispersion liquid of a charged particle known as a toner particle which generally consists of a coloring agent (for example, a pigment or a color) and a polymer binder. A charge director may contain the liquid development liquid component added in order to adjust the polarity of the charge on a toner particle, and magnitude.

[0007] A liquid toner is divided into two kinds. For convenience, since it is divided into a usual liquid toner and an organosol toner and an organosol toner is [among these] excellent in stability, this is more desirable in the electrophotography field.

[0008] The stable organosol contains the colloidal particle (diameter: 0.1-1 micrometer) of a polymer binder. Generally the above-mentioned particle is compounded by the nonaqueous solubility distribution polymerization with a low dielectric hydrocarbon solvent. He was fastidious, and an organosol particle is adsorbed physically or is stable in three dimensions, without condensing for the activity of a soluble polymer by which the graft was carried out chemically. The most general nonaqueous solubility distribution polymerization method is a free radical polymerization which carries out one or more [of the ethylene partial saturation monomers (for example, an acrylic acid or a methacrylic-acid monomer) dissolved in a hydrocarbon medium] at the time of the polymerization under existence of a prior shaping amphiphilic polymer. A prior shaping amphiphilic polymer is a stabilizer and this consists of two peculiar units. The 1st unit is intrinsically insoluble to a hydrocarbon medium, and the 2nd unit is freely dissolved in a hydrocarbon

medium.

[0009] If a monomer converts little by little and reaches critical molecular weight by implementation of the polymerization reaction for manufacturing an organosol particle, it will separate into a precipitate gestalt from a solution across the limitation of the solubility, and a polymer will form a "core" particle. A core is adsorbed, or the amphiphilic polymer forms covalent bond, and by this, a core grows and forms a discrete particle. A particle grows and continues until a monomer is lost, and it enables it to stabilize the amphiphilic polymer "shell" to which the core adhered in three dimensions, without a growth core particle condensing. Thus, as for the formed nonaqueous solubility colloidal dispersion liquid (organosol), a number average diameter contains the core / shell polymer particle of 0.1-0.5-micrometer range.

[0010] Then, the above-mentioned organosol can carry out simple installation of a coloring agent pigment and the charge director, or can mix them, and can make a liquid toner by passing through the processing process by the well-known mixed means effective for contracting particle magnitude by the reduction process or the technical field concerned of high shear homogenization, ball milling, ***** milling, high energy bead (sand) milling, or other particle magnitude at the time of dispersion-liquid formation.

[0011] If mechanical energy is added to dispersion liquid at the time of milling, pigment floc will be made to a primary particle (diameter of 0.05-1.0 micrometers), the role which grinds an organosol to a fragment so that it can adhere to the pigment front face formed newly is carried out, and it is made for the pigment particle stabilized in three dimensions not to condense.

[0012] The electrified nonaqueous solubility pigment dispersion liquid stabilized in three dimensions as a result including the particle which has the number average diameter of 0.1-2.0 micrometers are obtained, and a number average or the weighted mean particle diameter of a toner particle is 0.1-0.5 micrometers in these dispersion liquid. Thus, the dispersion liquid stabilized in three dimensions are suitable for the high resolution print.

[0013] Electrification of liquid ink changes dramatically with pigments. The so-called "charge modifier" and the charge director known are required to adjust an ink conductivity value to an allowed value, and these contents completely change with coloring agent pigments, and are designed by the well-known charge director design principle in ink. The ink containing the coloring agent pigment which is different from each other acts so that it may differ dramatically under the printing conditions of making it expose by high electric field etc. The change based on the electrification property that a coloring agent pigment is different from each other is not desirable. Moreover, although it must be careful about the lot-to-lot variable of a coloring agent pigment, it is because the lot-to-lot variable of a coloring agent pigment causes change which is not desirable in the property of ink. Therefore, it is desirable to have ink which has conductivity and electrical characteristics regardless of the type or lot of a coloring agent pigment.

[0014] Moreover, if black ink with a charge director's small content is especially used with the present ink constituent, ink with few charge director contents and the printed optical density can be reduced, and the trouble (trouble widely recognized to be a side effect with the image formation process) of exaggerated tones, such as tailing, wash-off, and sludging, can be reduced. The efforts for manufacturing efforts, i.e., ink excellent in conductivity, raising the charge organization potency force of ink for effective image formation, even if it reduces a charge director content do not have effectiveness in raising the charge organization potency force, or cause the result which is not desirable as for high free phase conductivity etc. This is defined by the section under toner conductivity and is a well-known property in the liquid electrophotography field.

[0015] The useful charge director of recent years most has the solubility property restricted with the low dielectric constant solvent suitable for electrophotography liquid ink. Consequently, a charge director condenses, as it distributed under the binder of the particle distributed from the liquid, or liquid ink. There is almost no direct physical contact or direct interaction between a coloring agent pigment and a charge director as a result, and an ink imprint is performed in inefficient under the imprint process promoted in static electricity.

[0016] The technique for improving the distributed stability and the charge property of liquid ink is indicated by the following reference.

[0017] The liquid ink containing the block copolymer which has the 1st block which contains the distributed pigment, and a nitrogen content aromatic series vinyl compound and a non-nitrogen aromatic series vinyl compound in the United States patent official report No. 4,665,011, and the 2nd block containing polymerization nature C4-C6 diene is indicated. It is reported that these liquid ink has the outstanding distributed stability and charge stability.

[0018] According to the United States patent official report No. 5,009,980, the thermoplastic binder of an electrification adjuvant is made to distribute substantially insolubility or the aromatic series nitrogen content compound which is not mixed on a nonpolar liquid carrier, and the liquid ink which has the improved image quality is formed.

[0019] According to the United States patent official report No. 4,061,582, poly vinyl acetate is used as a binder and

oating is carried out to the front face of a coloring agent pigment particle. The stable liquid ink which has oleophilic by which the processed pigment particle has improved through the minimum milling process] is produced.

0020]

Problem(s) to be Solved by the Invention] However, it is not indicated by the above-mentioned reference especially about the content which uses a nitrogen content polymer for the coloring agent pigment by which surface treatment was carried out.

0021] Therefore, even if electrification nature of the object [1st] of this invention improves and it uses a small amount of charge accommodation additive by including the coloring agent by which surface treatment was carried out by the nitrogen content polymer, it is to offer liquid ink excellent in the conductivity property.

0022] Moreover, the 2nd object of this invention is to offer the manufacture approach of the above-mentioned liquid ink.

0023]

Means for Solving the Problem] In order to solve the above-mentioned technical problem, in the 1st viewpoint of this invention, the liquid ink characterized by including the coloring agent by which surface treatment was carried out by the carrier liquid, the organosol, and the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer is offered.

0024] Moreover, in order to solve the above-mentioned technical problem, it sets in the 2nd viewpoint of this invention. The phase which dissolves the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer in a solvent, and forms a polymer solution, (a-1) The phase which distributes a color particle in the above-mentioned polymer solution, and forms coloring agent dispersion liquid, (b-1) (c-1) The manufacture approach of the liquid ink characterized by including the phase which forms the color particle which removed some solvent at least and was processed from the above-mentioned coloring agent dispersion liquid, and the phase of making a carrier liquid content organosol distributing the coloring agent by which processing was carried out [above-mentioned (d-1)] is offered.

0025] Moreover, in order to solve the above-mentioned technical problem, it sets in the 2nd viewpoint of this invention. The phase which dissolves the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer in a solvent, and forms a polymer solution, (a-2) The phase which distributes a color particle in the above-mentioned polymer solution, and forms coloring agent dispersion liquid, (b-2) (c-2) The manufacture approach of the liquid ink characterized by including the phase of carrying out the sediment of the color particle processed from the above-mentioned coloring agent dispersion liquid, and the phase of making a carrier liquid content organosol distributing the color particle by which processing was carried out [above-mentioned (d-2)] is offered.

0026] Moreover, as for the nitrogen of the above-mentioned nitrogen content polymerization nature monomer, in the above-mentioned liquid ink and this manufacture approach, it is desirable to exist in the group chosen from the group which consists of an amide (amide), an amide (amido), amino, and an amine group.

0027] And as for the above-mentioned nitrogen content polymerization nature monomer, it is desirable that it is, or more [it was chosen from the group which consists of the methacrylate which has an aliphatic series amino radical or acrylate, a nitrogen content heterocycle vinyl monomer, the annular amide monomer by which N-vinyl permutation was carried out, an ethylene monomer by which nitrogen radical content aromatic substitution was carried out, and a nitrogen content vinyl ether monomer] one.

[0028] At this time, the methacrylate or acrylate which has the above-mentioned aliphatic series amino radical N and N-dimethylaminoethyl (meta) acrylate, N and N-diethylaminoethyl Acrylate, N, and N-dibutyl aminoethyl (meta) acrylate, N, and N-hydroxyethylamino (meta) acrylate, N-benzyl-N-ethylamino (meta) acrylate, N, and N-dibenzyl aminoethyl (meta) acrylate (Meta) It is, or more [it was chosen from the group which consists of N-octyl, N, and N-dihexyl aminoethyl (meta) acrylate] one. And the above-mentioned nitrogen content heterocycle vinyl monomer N-vinyl imidazole, N-vinyl indazole, N-vinyl tetrazole, 2-vinyl pyridine, 4-vinyl pyridine, a 2-methyl-5-vinyl pyridine, 2-vinyl quinoline, 4-vinyl quinoline, 2-vinyl pyrazine, The annular amide monomer by which is or more [it was chosen from the group which consists of 2-vinyl oxazole and 2-vinyl benzooxazole] one, and N-vinyl permutation was carried out [above-mentioned] The ethylene monomer by which is or more [it was chosen from the group which consists of N vinylpyrrolidone, N-BINIRUPI ** RIDON, and N-vinyl oxazolidone] one, and nitrogen radical content aromatic substitution was carried out [above-mentioned] Dimethylamino styrene, diethylamino styrene, It is, or more [it was chosen from the group which consists of diethylamino methyl styrene and dioctylamino styrene] one. The above-mentioned nitrogen content vinyl ether monomer Vinyl-N-ethyl-N-phenylamino ethyl ether, vinyl-N-butyl-N-phenylamino ethyl ether, triethanolamine divinyl oxide, vinyl diphenylamino ethyl ether, the vinyl pyrrolidyl amino

ether, It is, or more [it was chosen from the group which consists of vinyl-beta-morpholino ethyl ether, an N-vinyl hydroxyethyl benzamide, and m-aminophenyl vinyl ether] one.

[0029] The dispersion liquid obtained from the above (b-1) and (b-2) a phase contain a charge director further. The above-mentioned charge director is the metal salt which consisted of organic anions which are polyvalent metal ion and counter ion. The above-mentioned polyvalent metal ion Ba (II), calcium (II), Mn (II), Zn (II), Zr (IV), Cu (II), aluminum (III), Cr (III), Fe (II), Fe (III), Sb (III), Bi (III), Co (II), La (III), Pb (II), Mg (II), Mo (III) and nickel (II), Ag (I), It is, or more [it was chosen from the group which consists of Sr (II), Sn (IV), V (V), and Y (III) and Ti (IV)] one. The above-mentioned organic anion It is, or more [it was chosen from the group which consists of a sulfonate guided from the carboxylate or aliphatic series sulfonic acid, and aromatic series sulfonic acid which are guided from any one of aliphatic carboxylic acid and aromatic carboxylic acid] one.

[0030] The above (a-1) and (a-2) the Cowley butanol numeric value of the solvent in a phase are 150 30 especially or more 30 or more, and it is desirable that the Cowley butanol numeric value of the above (d-1) and (d-2) the carrier liquid in a phase is 20 to especially less than 30 less than 30.

[0031] Moreover, as for especially the above-mentioned coloring agent, in liquid ink, it is desirable that it is a carbon black pigment.

[0032]

[Embodiment of the Invention] Hereafter, the gestalt of suitable operation of this invention is explained to a detail.

[0033] (Gestalt of the 1st operation) the surface treatment process of the coloring agent concerning this operation gestalt consists of phases of as a result drying an object, after coating a pigment front face, and namely, nitrogen content polymer sediment -- forming -- carrying out the sediment (it is coating about sediment) of the nitrogen content polymer especially under existence of a pigment or processing a coloring agent pigment with a nitrogen content polymer solution, a coloring agent and.

[0034] If the coloring agent pigment by which surface treatment was carried out is used, even if electrification extent improves further and uses a small amount of charge accommodation additive, the liquid ink which has a permissible conductivity value, and the pigment with which the effect of variables, such as a lot and a manufacturer, was reduced in the electrification property will be obtained.

[0035] The liquid ink constituent concerning this operation gestalt contains a carrier liquid, a coloring agent pigment, and an organosol. A coloring agent (especially pigment) is distributed by the mixture of a carrier liquid in this liquid ink constituent.

[0036] A film is formed promptly, without condensing and sedimenting (there being a quick self-process capability), and the ink constituent concerning this operation gestalt is especially useful at the xerography, IONO graph, or static electricity-image formation and other usual presswork.

[0037] As for a carrier fluid, in the above-mentioned ink constituent, it is desirable that it is chosen among well-known various matter by the technical field concerned, and especially the Cowley butanol (KB) numeric value uses less than (less than [Especially / 20 or more] 30) 30 thing. When KB numeric value of a carrier fluid separates from the above-mentioned range, since a graft stabilizer separates from the field which can be dissolved selectively, the role of a stabilizer cannot be played, an ink particle is not formed normally but the dispersibility and stability of an ink particle worsen, it is not desirable.

[0038] KB numeric value -- the ASTM testing method -- although measured by D1133-54T, this measuring method measures the addition tolerance of the hydrocarbon diluent in the 1-butanol solution of the Cowley numeric value of a standard solution. KB numeric value is expressed with the volume (ml) of a 25 degrees C [which is added to 20g of standard Cowley 1-butanol solutions, and can obtain predetermined turbidity] solvent.

[0039] As reference, although an examination value is shown about KB certified value, KB numeric value of toluene is 105 and KB numeric value of the mixture which consists of heptane 75% and toluene 25% is 40.

[0040] Generally the above-mentioned carrier liquid is oleophilic, is stabilized chemically and has insulation. "The liquid which has insulation" means the liquid which has a low dielectric constant and high electrical resistivity here. Dielectric constants are 1-5 five or less, and the dielectric constants of especially this insulating liquid are 1-3 more preferably. At this time, the electrical resistivity of a carrier liquid is more than 10⁹-ohmcm, and is 10¹⁰-10¹⁶-ohmcm more than 10¹⁰-ohmcm especially preferably.

[0041] There is no viscosity comparatively preferably, it is made for a charged particle to move at the time of development, and a carrier liquid can be suitably removed from the substrate with which volatility came out enough and the final image was formed. However, since a carrier liquid has non-volatile, it can minimize loss by a carrier liquid evaporating from a developer. Moreover, a carrier liquid must be inactive chemically to the matter used at a liquid electrophotography process or equipment especially a photo conductor, and its variant front face.

0042] As a concrete example of a carrier fluid, aliphatic hydrocarbon (n pentane, a hexane, heptane, etc.), alicyclic ring hydrocarbons (a cyclopentane, cyclohexane, etc.), aromatic hydrocarbon (benzene, toluene, xylene, etc.), the halogenated hydrocarbon solvents (the chlorinated alkane, the fluorinated alkane, chlorofluorocarbon, etc.), silicone oils, and these mixture can be mentioned. Especially as a carrier fluid, it is desirable that they are branching mold paraffin solvent mixture, such as trade name Isopar G (Isopar G), Isopar H, Isopar K, Isopar L, Isopar M, and Isopar V (Exxon Corporation), and it can mention aliphatic hydrocarbon solvent mixture, such as trade name NORUPA 12, NORUPA 13, and NORUPA 15 (Exxon Corporation), as most desirable carrier fluid.

0043] A graft stabilizer carries out the role which a core part and a graft reaction are caused [role] and stabilizes an ink particle.

0044] The constituent of a graft stabilizer is chosen so that the HIRUDE brand solubility variable of a graft stabilizer may approach with the thing of a carrier fluid and may generally become a pair etc., and a stabilizer is dissolved in a carrier solvent and it is fully solvated. Especially as a graft stabilizer, less than $1/2 \times 3.0\text{Mpa(s)}$, if the difference of a carrier liquid comparison HIRUDE brand solubility variable is 1.0 to less than $1/2 \times 3.0\text{Mpa(s)}$ polymerization nature compound, all have it. [usable] Moreover, if the differences of the effective HIRUDE brand solubility variable of an effective carrier liquid comparison stabilizer are especially less than $1/2 \times 3.0\text{Mpa(s)}$ from 1.0 less than $1/2 \times 3.0\text{Mpa(s)}$, as for a $1/2$ or more 3.0Mpa(s) polymerization nature compound, the difference of a carrier fluid comparison HIRUDE brand solubility variable will be used at the time of formation of a copolymer graft stabilizer.

0045] As for the absolute value difference of the HIRUDE brand solubility variable between a graft stabilizer (shell) and a carrier liquid, it is desirable that it is especially $1/2 \times 2.6 \text{ MPa}$ from 2.0.

0046] As a nonrestrictive example of a useful polymerization nature monomer, at the time of formation of a graft stabilizer 3, 3, 5-trimethyl cyclohexyl methacrylate, hexyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, dodecyl (lauryl) acrylate, octadecyl (stearyl) acrylate, BIHENIRU acrylate, Hexyl methacrylate, 2-ethylhexyl (methacrylate), [The indispensable condition of the C6-C30 acrylic acid containing DESHIRU methacrylate, dodecyl (lauryl) methacrylate, octadecyl (stearyl) methacrylate, isobornyl acrylate, and isobornyl methacrylate, methacrylic ester, and the above-mentioned solubility variable There are other acrylate and methacrylate to satisfy.

0047] It is chemically combined with the resin core (that is, the graft is carried out to the core), or a core is adsorbed and a graft stabilizer remains to the indispensable field of a resin core. Many reactions by which well-known was carried out to this contractor of the technical field concerned are effective for carrying out the graft of the soluble polymer stabilizer to an organosol core at the time of a free radical polymerization.

0048] Hydroxy ** in which the general graph TINGU approach has a partial saturation nature end group with run DAMUGU rafting of a polyfunctional free radical, the ring opening polymerization of the cyclic ether, ester, an amide, or acetal, and an epoxidation reaction includes the reaction, an esterification reaction (that is, glycidyl methacrylate reacts with a meta-grill acid, and advances the ester reaction under the Miyoshi amine catalyst) and a condensation reaction, or polymerization reaction of an amino chain migration agent.

0049] As for a graft stabilizer, it is desirable that number average molecular weight is 50,000-1,000,000dalton (Da), and it is 100,000-300,000Da most preferably 100,000 to 500,000 Da. Since a graft stabilizer separates from the field which can be dissolved selectively, and cannot perform the role of a stabilizer, an ink particle is not formed normally but the dispersibility and stability of an ink particle worsen when the number average molecular weight of a graft stabilizer separates from said range, it is not desirable.

0050] Moreover, the polydispersity of a graft stabilizer affects image formation and the imprint engine performance of a liquid toner. As for especially the polydispersity (ratio of the weight average molecular weight to number average molecular weight) of a graft stabilizer, generally, it is [15 or less / two to less than five] more preferably desirable 1-15, and that it is 2-2.5 most preferably.

0051] graph TINGU which forms a graph TINGU site -- law introduces a hydroxy group into a graft stabilizer at the time of a free radical polymerization, and makes all or a part of these hydroxy groups react in a consecutive non-free radical reaction phase under ethylene partial saturation nature aliphatic series isocyanate (example: meta-isopropyl dimethylbenzyl isocyanate [TMI]) or 2-SHIANATO ethyl methacrylate [IEM], and a catalyst And covalent bond of the graft stabilizer is carried out to the early insoluble acrylic-acid (j) polymer core through the reaction between the partial saturation vinyl group of a graph TINGU site, and an ethylene partial saturation core monomer (example: vinyl ester especially a with a carbon number of less than seven acrylic acid and methacrylic ester or vinyl acetate, vinyl system aromatic compounds, such as styrene, acrylic nitril, n-vinyl pyrrolidone, and vinyl chloride and vinylidene chloride) all over the consecutive free radical polymerization phase.

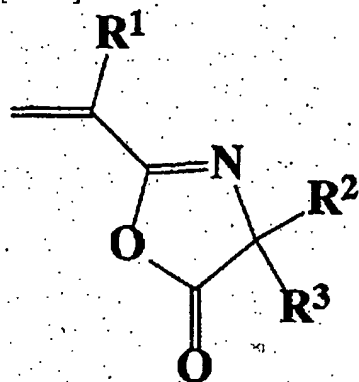
0052] When making an early insoluble core particle carry out graph TINGU of the prior shaping polymer stabilizer, other effective approaches are already well-known to this contractor of the technique concerned. For example, other

graph TINGU protocols are indicated by the reference of the Barrett dispersion-liquid polymerization (KE.J.Barrett, ed., John Wiley: New York, 1975, section 3.7-3.8, pp 79-106) in an organic medium. An approach especially useful although graph TINGU of the polymer stabilizer is carried out at a core is using a support group.

[0053] The above-mentioned support group offers the share ring of the core section of a particle, and the dissolution component of a solid stabilizer.

[0054] As a monomer including the above-mentioned support group An alkenyl azlactone comonomer, 2-hydroxyethyl methacrylate, 3-hydroxypropyl methacrylate and 2-hydroxyethyl acrylate, a pentaerythritol thoria chestnut rate, 4-hydroxy butyl vinyl ether, The 2-alkenyl -4 which has the addition product and the following structure expression between partial saturation nature nucleophilicity objects including hydroxy, amino or mercaptan groups, such as 9-octadecene-1-ol, cinnamyl alcohol, allyl mercaptan, and meta-allylamine, Azlactones, such as 4-dialkyl azlactone, are suitable.

[0055]



[0056] the inside of the above-mentioned formula, and R1 -- the alkyl group of H or C1-C5 -- desirable -- the alkyl group of C1 -- it is -- R2 and R3 -- the low-grade alkyl group of each C1-C8 -- it is the low-grade alkyl group of C1-C4 preferably.

[0057] A graph TINGU mechanism is ethylene partial saturation nature isocyanate (example: carried out to the hydroxy group which introduced dimethyl-m-isopropanal ** nil benzyl isocyanate (American Cyanamid) into the graft stabilizer precursor (namely, hydroxyethyl methacrylate) before by carrying out graph TINGU.) most preferably.

[0058] A core polymer is performed by INSAICHU by the copolymerization reaction with a stabilizer monomer. forming the ink constituent which the constituent of an insoluble resin core is adjusted preferentially, expresses glass transition temperature (Tg) with a low resin core, and contains resin as a principal component -- the temperature more than the glass Tg of a core -- it is adjusted so that a film may be preferably formed promptly at an elevated temperature from 23 degrees C or this (self-immobilization is made quickly). Quick self-immobilization is a fault at the time of printing (for example, contamination and an imprint imperfect at the time of trailing-edge trailing and high-speed printing are prevented beforehand.). Core Tg has desirable less than 23 degrees C, and less than 10 degrees C is less than -10 degrees C most preferably.

[0059] As a nonrestrictive example of the polymerization nature organic compound suitable for an organosol core Methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, N, and N-dimethylaminoethyl (meta) acrylate, N, and N-diethylaminoethyl Acrylate, N, and N-dibutyl aminoethyl (Meta) Acrylate, M, N-hydroxyethyl aminoethyl (Meta) Acrylate, N-benzyl, N-ethylamino ethyl (Meta) Acrylate, N, and N-dibenzyl aminoethyl (meta) acrylate, N-octyl, N, and N-diethyl aminoethyl (meta) acrylate, N-vinyl imidazole (N-vinylimidazole), (Meta) N-vinyl indazole, N-vinyl tetrazole, 2-vinyl pyridine, 4-vinyl pyridine, a 2-methyl-5-vinyl pyridine, 2-vinyl quinoline, 4-vinyl quinoline, 2-vinyl pyrazine, 2-vinyl oxazole, 2-vinyl benzoxazole, N vinylpyrrolidone and N-BINIRUPI ** RIDON, N-vinyl oxazolidone, N-methylacrylamide, N-octyl acrylamide, N-phenyl methacrylamide, N-cyclohexyl acrylamide, Acrylamides (meta), such as N-phenylethyl acrylamide, N-p-methoxy-phenyl acrylamide, acrylamide, N,N-dimethylacrylamide, N, and N-dibutyl acrylamide, N-methyl, and N-phenyl acrylamide PI ** lysine acrylate, morpholine acrylate, Dimethylamino styrene, diethylamino styrene, diethylamino methyl styrene, dioctylamino styrene, vinyl-N-phenylamino ethyl ether, vinyl-N-butyl-N-phenylamino ethyl ether, Triethanolamine divinyl oxide, vinyl diphenylamino ethyl ether, the vinyl pyrrolidyl amino ether, vinyl-beta-morpholino ethyl ether, N-vinyl hydroxyethyl benzamide, m-aminophenyl vinyl ether and other acrylate systems and methacrylate -- there are monomers, such as methyl methacrylate, ethyl acrylate, and dimethylaminoethyl methacrylate, most preferably.

[0060] Although other polymers are independent or it may be used with the above-mentioned matter, he is fastidious and there are a melamine and melamine-formaldehyde-resin, phenol-formaldehyde-resin, epoxy resin, polyester resin, styrene and styrene / acrylic-acid copolymer, vinyl acetate and vinyl acetate / acrylic-acid copolymer, acrylic-acid and methacrylic ester, cellulose acetate, and cellulose acetate-butyrate copolymer and a Pori (vinyl BUCHIRARU) copolymer as a concrete example of a polymer.

[0061] The optimal weight ratio of a resin core and stabilizer shell is 1:1 to 15:1, are 2:1-10:1 preferably, and are 4:1-8:1 most preferably. When a core / shell ratio separates from the above-mentioned range, the effectiveness which is not desirable is acquired. For example, if a core / shell ratio exceeds 15, the graft stabilizer for making it stabilize in three dimensions, without an organosol condensing is inadequate. On the other hand, since the driving force of a polymerization reaction is inadequate with [a core / shell ratio] one [less than], the copolymer solution with which another particle phase which is not organosol dispersion liquid by which shell was stabilized was formed is formed.

[0062] The magnitude of the particle in an organosol does effect like a desiccation process and an imprint fault like the image formation fault of liquid ink. Preferably, it is 0.05-5.0 micrometers, and the magnitude (dynamic light scattering is determined) of the primary particle of an organosol is 0.15-1 micrometer, and is 0.20-0.50 micrometers.

[0063] The liquid ink using the above-mentioned organosol contains the coloring agent contained in thermoplastic organosol resin.

[0064] If it is a coloring agent well-known at the technical field concerned as the above-mentioned coloring agent, all are useful and matter, such as a color, a stain, and a pigment, is included.

[0065] The desirable coloring agent and desirable pigment which are introduced into polymer resin are useful to usually having insolubility and refractoriness to a carrier liquid, and making a latent-image static electricity-image visualize, and effective for it. As a nonrestrictive example of such a coloring agent, a copper phthalocyanine blue (C. I. Pigment Blue 15:1, 15:2, 15:3 and 15:4), Mono-ant RIDOI yellow (C. I. Pigment yellow 1, 3, 65, 73, and 74), PARIRIDO yellow (C. I. Pigment yellow 12, 13, 14, 17, and 83), Allyl compound amide (Hansa) yellow (C. I. Pigment yellow 10, 97, 105, and 111), Azo red (C. I. Pigment Red 3, 17, 22, 23 and 38, 48:1, 48:2, 52:1, 81 and 179), The Quinacridone Magenta (C. I. Pigment Red 122, 202 and 209), There are black pigments, such as differential-sized carbon Cabot Monarch 120, Cabot Regal 300R, Cabot Regal 350R, Vulcan X72), etc.

[0066] By the toner particle, the optimal weight ratios of resin and a coloring agent are 1:1-20:1, are 3:1-10:1 preferably, and are 5:1-8:1 most preferably. Generally the content of the total distributed matter in a carrier fluid is 0.5 - 70 % of the weight on the basis of the total liquid development liquid constituent, is 1 - 25 % of the weight preferably, and is 2 - 12 % of the weight most preferably.

[0067] If surface treatment of the coloring agent pigment is carried out using a nitrogen content polymer or a copolymer, it makes the charge organization potency force improve, and can reduce electrification change.

[0068] As a nitrogen content polymer or a copolymer, N and N-dimethylaminoethyl (meta) acrylate, N and N-diethylaminoethyl Acrylate, N, and N-dibutyl aminoethyl (Meta) Acrylate, N, and N-hydroxyethylamino (Meta) (Meta) Aliphatic series amino radicals, such as acrylate, N-benzyl-N-ethylamino (meta) acrylate, N, and N-dibenzyl aminoethyl (meta) acrylate, N-octyl, N, and N-dihexyl aminoethyl (meta) acrylate Have. An acrylate system, N-vinyl imidazole and N-vinyl indazole, N-vinyl tetrazole, 2-vinyl pyridine, 4-vinyl pyridine, a 2-methyl-5-vinyl pyridine, 2-vinyl quinoline, 4-vinyl quinoline, (Meta) Nitrogen content heterocycle vinyl monomers, such as 2-vinyl pyrazine, 2-vinyl oxazole, and 2-vinyl benzoxazole, The annular amide monomer; N-methylacrylamide by which N-vinyl permutation was carried out, such as N vinylpyrrolidone, N-BINIRUPI ** RIDON, and N-vinyl oxazolidone, N-octyl acrylamide, N-phenyl methacrylamide, N-cyclohexyl acrylamide, N-phenylethyl acrylamide, N-p-methoxy-phenyl acrylamide, acrylamide, N,N-dimethylacrylamide, N, and N-dibutyl acrylamide, N-methyl, N-phenyl acrylamide, PI ** lysine acrylate, Morpholine acrylate etc. Acrylate; (Meta) The ethylene monomer containing nitrogen radicals, such as dimethylamino styrene, diethylamino styrene, diethylamino methyl styrene, and dioctylamino styrene, by which aromatic substitution was carried out; Vinyl-N-ethyl-N-phenylamino ethyl ether, Vinyl-N-butyl-N-phenylamino ethyl ether, triethanolamine divinyl oxide, vinyl diphenylamino ethyl ether, the vinyl pyrrolidyl amino ether, vinyl-beta-morpholino ethyl ether, The nitrogen content polymerization nature organic compound chosen from the group which consists of nitrogen content vinyl ether monomers, such as N-vinyl hydroxyethyl benzamide and m-aminophenyl vinyl ether, can be mentioned.

[0069] The above-mentioned polymer must contain at least 1%, at least 2%, at least 5%, at least 8%, at least 10%, or at least 15% of nitrogen content polymerization nature organic compound as mol criteria of a polymerization unit by the polymer containing a nitrogen atom. As for a nitrogen atom, it is desirable that they are a part of an amide (amide), amide (amido), amino, or amine radical, and it is not desirable that they are a part of nitroglycerine or cyano substituent.

[0070] Surface treatment of a coloring agent pigment can be carried out by the general approach well-known as a surface treatment method of a particle by the technical field concerned. As a nonrestrictive example of such a surface-preparation approach, there are the milling or the kneading method, ion penetration method, and flash plate approach of a pigment under solution coating and the drying method, a powder coating method, the approach of carrying out sediment on a pigment front face, a nitrogen content polymer, or copolymer existence.

[0071] Especially a solution coating method is performed when the Cowley butanol numeric value dissolves a nitrogen content polymer or a copolymer in the polar solvent of 30-150 30 or more. As an example of the solvent for a nitrogen content polymer or copolymers, there are a tetrahydrofuran, an acetone, a methyl ethyl ketone, alcohol, water, a methanol, etc. And a coloring agent pigment is added and it is distributed by other well-known means effective in reduction of the particle magnitude in dispersion liquid in high shear mixing, high shear homogenization, ball milling, ***** milling, high energy bead (sand) milling, or the technical field concerned. If mechanical energy is added to dispersion liquid at the time of milling, coloring agent pigment floc can be ground in smaller particle magnitude.

[0072] Then, the coloring agent pigment particle processed by removing a solvent from coloring agent pigment dispersion liquid by the well-known drying method in the technical fields concerned, such as oven, vacuum oven, evaporation, distillation, a spray drying machine, a microwave oven, and an infrared evaporation system, is formed.

[0073] After the Cowley butanol numeric value dissolves a nitrogen content polymer or a copolymer with the polar solvent of 30-150 30 or more, especially the approach of carrying out sediment on a pigment front face adds a coloring agent pigment, and other well-known means effective for reduction of the particle magnitude in dispersion liquid distribute this in high shear mixing, high shear homogenization, ball milling, ***** milling, high energy bead (sand) milling, or the technical field concerned. And a non-solvent is added and the front face of a coloring agent pigment is coated with sediment of a nitrogen content polymer or a copolymer.

[0074] All can be used for a non-solvent if a nitrogen content polymer is the liquid seldom dissolved. A non-solvent is chosen by a polar solvent and a nitrogen content polymer, or the copolymer.

[0075] A flash plate approach is kneaded or mixed with the resin solution in the condition that the water which covers each pigment particle front face was permuted by the resin solution, in water-soluble pigment dispersion liquid. This pigment sample by which flash plate processing was carried out is usable as dispersion liquid in drying. The above-mentioned resin concerning this operation gestalt is a nitrogen content polymer or a copolymer.

[0076] It will be as follows if the two typical manufacture approaches of the liquid ink concerning this operation gestalt are investigated with reference to the surface treatment approach of the above-mentioned coloring agent pigment.

[0077] The 1st manufacture approach is the thing of an about when especially the front face of a pigment is processed with the above-mentioned solution coating method, a coloring agent and.

[0078] First, the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer is dissolved in a solvent, and a polymer solution is formed. Subsequently, a coloring agent pigment particle is distributed in the above-mentioned polymer solution, and coloring agent pigment dispersion liquid are formed.

[0079] Then, the coloring agent pigment particle which removed some solvent at least and was processed from the above-mentioned coloring agent pigment dispersion liquid is formed, and the liquid ink concerning this operation gestalt is completed by making a carrier liquid content organosol distribute the coloring agent pigment particle by which surface treatment was carried out in this way.

[0080] The 2nd manufacture approach is enforced by the approach of carrying out the sediment of the polymer containing the unit guided to the above-mentioned pigment front face from at least one nitrogen content polymerization nature monomer at the time of the surface treatment of a coloring agent (especially pigment).

[0081] First, the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer is dissolved in a solvent, a polymer solution is formed, a coloring agent pigment particle is distributed in the above-mentioned polymer solution, and coloring agent pigment dispersion liquid are formed.

[0082] The liquid ink concerning this operation gestalt is completed by settling the coloring agent pigment particle processed from the coloring agent pigment dispersion liquid formed of the above-mentioned process, and making a carrier liquid content organosol distribute the color particle by which processing was carried out [above-mentioned].

[0083] On the other hand, an electrophotography liquid toner introduces a charge modifier into liquid ink, and makes it. The charge modifier known as the so-called "charge director" provides a toner particle with a uniform charge polarity.

[0084] A charge director is introduced into a toner particle by the approach with various approaches of chelating to functional groups, such as an approach to which a toner particle is made reacting chemically with a charge director, a method of making a toner particle adsorbing a charge director physically or a stabilization group, an antioxidation nature group, and a charge refining group, approaches of introducing solubility, undissolved, or an emulsifiability group into a toner particle, etc. A desirable approach is making a graft stabilizer using a functional group. A charge

director plays the role which gives the charge of a predetermined polarity of a toner particle, and all are usable if he is a charge director in the technical field concerned. For example, a charge director can introduce into the gestalt of the metal salt which consisted of organic anions as polyvalent metal ion and counter ion.

[0085] As the above-mentioned metal ion, Ba (II), calcium (II), Mn (II), Zn (II), Zr (IV), Cu (II), aluminum (III), Cr (III), Fe (II), Fe (III), Sb (III), Bi (III), Co (II), La (III) and Pb (II), Mg (II), Mo (III), nickel (II), Ag (I), Sr (II), Sn (IV), V (V), Y (III), Ti (IV), etc. are suitable. As the above-mentioned organic anion Aliphatic series or the carboxylate derived from aromatic carboxylic acid or a sulfonic acid or a sulfonate -- there are aliphatic series fatty acids, such as stearic acid, behenic acid, a neo decanoic acid, diisopropyl salicylic acid, an octanoic acid, an abietic acid, a naphthenic acid, a lauric acid, and the Tallinn acid, preferably.

[0086] the metal carboxylate (soap) indicated by the U.S. Pat. No. 3,411,936 number as reference in this operation gestalt as a desirable positive charge director -- it is -- this -- at least -- the alkaline earth metals of the fatty acid of a carbon number 6-7 and a heavy-metal salt, and naphthenic-acid content ring aliphatic series **** -- it is polyvalent metal soap of a zirconium and aluminum more preferably, and is zirconium soap (Zirconium HEX-CEM and Mooney Chemicals) of an octanoic acid most preferably.

[0087] The desirable charge direction level used for a toner constituent changes with many factors containing the ratio of reclamation of a graft stabilizer and an organosol, the molecular weight of an organosol, the particle magnitude of an organosol, the core / shell ratio of a graft stabilizer, the pigment for toner manufacture, and an organosol and a pigment. Moreover, desirable charge direction level changes with designs of the essence like an electrophotography image formation fault especially development hardware, and a photosensitive element. However, if it is this contractor of the technical field concerned, it will adjust so that the result which asks for the level of the charge direction based on the above-mentioned variable in each application can be obtained.

[0088] The conductivity of a liquid toner is clearly established by the efficiency metrics of the toner in an electrophotography image by the technical field concerned. In addition, the useful conductivity range is 1.0×10^{-11} - 10.0×10^{-11} mho/cm.

[0089] That the conductivity of a liquid toner is high means things, if a charge forms a crowd on a toner particle at imperfection. This is understood from the relation between current density and the toner accumulated at the time of development not being not much close.

[0090] On the other hand, the toner particle is not charged or that the conductivity of a liquid toner is low means that there is almost nothing. This causes a very low development rate.

[0091] Generally it is well-known to use a charge director compound so that electrification of each particle may fully be performed. In recent years, the data that many unnecessary charges located in the electrification kind of the liquid in a carrier fluid existed became clear in the approach of using a charge director. Thus, an unnecessary charge makes development inefficient-wise, instability-wise, and in being un-consistent.

[0092] In this operation gestalt, the charge was made to exist locally on a toner particle, it prevented substantially that a charge moved to a liquid from this particle, and the above-mentioned trouble has been substantially improved greatly by [it is made for other unnecessary charge components not to exist in a liquid] endeavoring.

[0093] As criteria of the property demanded, these researchers use the ratio of the conductivity of the carrier liquid shown with a liquid toner, and the conductivity (toner dispersion liquid constituted thoroughly) of a general liquid toner. this ratio -- less than 0.6 -- especially -- 0.01 to 0.6 -- desirable -- 0.01 to 0.4 -- and it is 0.01-0.3 most preferably. Other above-mentioned conventional toners have a larger ratio than this in the 0.95 range.

[0094] Various approaches are used for reducing the particle magnitude of a pigment at the time of manufacture of a gel liquid toner. The approach which used other well-known means as a suitable approach by high shear homogenization, ball milling, ***** milling, high energy bead (sand) milling, or the technical field concerned is mentioned.

[0095] Generally by the xerography, the static electricity-image (1) photosensitivity element One or more phases are minded for the phase of electrifying homogeneity in applied voltage, the phase which some (2) photosensitivity elements are exposed and electrified with a radiation supply source, and forms a latent-image image, the phase which adds (3) toners to a latent-image image, and forms a hue image, and (4) hue image. A photosensitive element is formed on the sheet by which coating was carried out, a drum, or a belt by passing through the phase imprinted on the last television object sheet. As for a hue image, for other applications, it is desirable to make it fix at the heated pressure roller or the technical field concerned using other well-known fixed approaches.

[0096] One static electricity-charge is positive charge or a negative charge among a toner particle or a photosensitive element, and the electrophotography process in this operation gestalt is performed by distributing a charge on the photosensitive element preferably charged with positive charge.

[0097] Furthermore, the toner charged with positive charge joins the field to which positive charge was distributed using the liquid toner charge development technique. This development process is performed by the uniform electric field formed with the development electrode located near the photosensitive element front face. Bias voltage is impressed to an electrode in the medium magnitude of an initial electrification surface electrical potential difference and an exposure surface voltage level.

[0098] An electrical potential difference is adjusted so that the tone playback scale for halftone dots can be obtained without the maximum consistency level demanded and the background accumulated.

[0099] A liquid toner flows between an electrode and photosensitive elements. The electrified toner particle is fluid at electric field, and it adheres to it to the electrification field of a photosensitive element, and does not adhere to it in the field in which a non-charged image is not formed. The liquid toner of the excess amount which remains to a photosensitive element is removed by the well-known approach by the technical field concerned. Then, it is made to dry or a photosensitive element front face is made to be dried under room temperature conditions.

[0100] Two variables estimate the quality of liquid ink.

[1] Conductivity (2) which is ink Stability of ink with time [0101] The ink concerning this operation gestalt has little conductivity change by this, when it excels in conductivity on low current director level and a coloring agent pigment is changed. The ink concerning especially this operation gestalt forms a high resolution and high-speed multi-color image, when it is combined with a reversal double layer photo conductor and used at a liquid charge development electrophotography process.

[0102] Its all are usable if the substrate which televises an image from a photosensitive element is the common television object matter like paper, coating paper, a polymer film, and the first stage or the polymer film by which coating was carried out. Moreover, the front face covered with the metal or metal which coating was specially carried out or was processed is usable as a television object. A polymer film contains the plasticized poly vinyl chloride (PVC) which was reached and blended, an acrylic-acid system, a polyurethane system, polyethylene / acrylic-acid copolymer, and poly vinyl BUCHIRARU. Moreover, an available composite is commercially [Scotchcal, Scotchlite, Panaflex (trade name), etc.] useful at the time of substrate manufacture.

[0103] The process in which a final television object or an imprint medium is made to imprint the image formed from the electrification front face introduces the variant promoting agent in the particulate material used in order to form an image, and improves. If the silicon content matter or the fluorine content matter is introduced into the external (shell) layer of a particle, the effective imprint of an image will be promoted.

[0104] It sets like a multicolor image formation fault, and the sequence is not restricted specially but a toner joins the front face of a dielectric element or a photosensitive element. However, it is desirable to take into consideration the point that reversal takes place, and to add an image in special sequence with the transparency and reinforcement of a color for a coloring-reason, at the time of an imprint. For example, the sequence that a more direct image formation fault is as desirable as a double imprint fault is the order of yellow, a Magenta, cyanogen, and black. Moreover, desirable sequence is the order of black, cyanogen, a Magenta, and yellow at a single imprint process. In order that yellow may generally avoid the contamination from other toners, an image is formed first, and since a black toner generally acts as a filter of an exposure supply source, finally black forms an image.

[0105] The conductivity value for using liquid ink most efficiently is 50-1200pico. It is the range of mho-cm -1. The liquid ink manufactured by the approach concerning this operation gestalt is 500 from the case of the dispersion liquid which contain % of the weight of a solid-state 2.5%, 100 [for example,],pico. It is mho-cm -1.

[0106] Selectively, the process which carries out over coating of the imprint image carries out an image in order to protect physical breakage and/or chemical-rays breakage. The over coating constituent is well-known at the technical field concerned, and contains the polymer for polymer film formation which was generally dissolved in the volatile solvent or floated. An ultraviolet-rays optical absorption agent may be selectively added to the above-mentioned coating constituent. Moreover, the approach of carrying out the lamination of the image protective layer to the front face in which the image was formed is well-known at the technical field concerned, and the approach of starting is used in this operation gestalt.

[0107] Hereafter, the example concerning this invention is explained. In addition, this invention is not limited to this example.

[0108]

[Example] A chemistry abbreviation and the glossary following raw material of a chemical source are used for the polymer manufacture approach of this example.

[0109] The catalysts used by this example are azobisisobutyronitril (trade name VAZO-64 which came to hand from azobisisobutyronitril and DuPont Chemical), and dibutyltin dilaurate (Dibutyl Tin Dilaurate) (DBTDL, Aldrich

Chemical Co.). A monomer is Scientific unless reference is made specially. Polymer It is available from Product and nc.

[0110] The monomer of this example is displayed in the following abbreviation.

[0111] dimethyl-m-isopropanal ** nil benzyl isocyanate (TMI and CYTECInductries); -- ethyl acetate (EA); 2-hydroxyethyl methacrylate (EHMA); -- 2-hydroxyethyl methacrylate (HEMA); and methyl methacrylate (MMA)

[0112] The analysis test approach following test approach is used in order to evaluate the polymer in this operation gestalt, and the property of ink.

[0113] The solid-state content in a graft stabilizer, an organosol and the solid-state content graft stabilizer solution in a liquid toner, an organosol, and ink dispersion liquid carried out gravimetric analysis using halogen lamp desiccation oven with a precision analysis balance (Mettler Instruments Inc.). The solid-state content was respectively measured by about 2g sample using the sample dry downing method.

[0114] Various properties of a graft stabilizer molecular weight graft stabilizer are important for the engine performance of the stabilizer containing molecular weight and molecular weight polydispersity. Generally graft stabilizer molecular weight is displayed with weight average molecular weight (Mw), and molecular weight polydispersity is displayed by the ratio (Mw/Mn) of weight average molecular weight and number average molecular weight. Although the molecular weight variable of a graft stabilizer is determined by gel permeation chromatography (GPC), as a carrier solvent, a tetrahydrofuran is used at this time. Absolutely, Mw was determined by the Dawn DSP-F light-scattering detector (Dawn DSP-Flight scattering detector) (Wyatt Technology Corp.), and the rate of a part for Mn measurement and Mw measured value estimated polydispersity using the OPUCHIRABU (optilab) 903 differential-refractometer detector.

[0115] Liquid toner property In order to evaluate the property of a liquid toner, physical and direct assessment of the image quality acquired by measuring chemical property and developing a toner by the LEP image formation mechanism of a toner is required.

[0116] The measured toner property can be divided roughly into a magnitude related characteristic (particle magnitude) and an electrification related characteristic (bulk and free phase conductivity, dynamic mobility, and F-potential).

[0117] Distribution of particle magnitude toner particle magnitude was measured using the analyzer (Horiba LA-900 laser diffraction particle size analyzer) (Horiba Instruments, Inc.) of Horiba LA-900 laser diffraction particle magnitude. The toner sample was diluted with about 1/500 volume ratio, and was ultrasonicated for 1 minute by 150W and 20kHz before measurement. Toner particle magnitude is expressed with the number average base so that the role of the directions person of the basic (primary) particle magnitude of an ink particle may be performed.

[0118] Toner conductivity liquid toner conductivity (bulk conductivity, kb) was measured by about 18Hz using SAIENTIFIKA model 627 conductometry equipment (Scientifica model 6277 conductivity meter) (Scientifica Instruments, Inc.). Moreover, free (dispersant) phase conductivity (kf) was measured without the toner particle. The toner particle was made to separate from a liquid environment by carrying out centrifugal separation at 6,000rpm (6,110 relative centrifugal force) and 5 degrees C with a Joan (Jouan) MR1822 centrifugal-separation vessel (Winchester, VA) for 1 to 2 hours.

[0119] The floating liquid was moved carefully and the conductivity of this liquid was measured using SAIENTIFIKA model 627 conductometry equipment. The free phase conductivity percent to bulk toner conductivity was measured at 100% (kf/kb).

[0120] Particle mobility toner particle electrophoretic mobility (dynamic mobility) was measured using the MATEKKU MBS-8000 **** supersonic-wave amplitude analysis apparatus (Matec MBS-8000 Electrokinetics Sonic Amplitude Analyzer; Matec Applied Sciences, Inc.). Unlike the electrokinetics measurement based on detailed electrical-and-electric-equipment migration, MBS-8000 analysis apparatus has the advantage that it is not necessary to dilute the toner sample for acquiring a mobility value. Therefore, the dynamic mobility of a toner particle can be actually measured by desirable solid-state concentration at the time of printing.

[0121] MBS-8000 analysis apparatus measures the reaction of the charged particle in high-frequency (1.2MHz) alternating current (AC) electric field. At high-frequency AC electric field, a supersonic wave arises on the same frequency of impression electric field by relative migration between an electrification toner particle and the surrounding quality of a dispersion medium (counter ion content). It is measurable in the amplitude of a 1.2MHz supersonic wave using a piezoelectric quartz converter. This **** supersonic-wave amplitude (ESA) is in direct proportion to the low electric-field AC electrical-and-electric-equipment mobility of a particle. Furthermore, particle F-potential is calculable with the above-mentioned equipment from dynamic mobility measured value and well-known toner particle magnitude, dispersant liquid viscosity, and a liquid dielectric constant.

[0122] The mixture of NORUPA 12 (trade name) (2561g), EHMA (849g), 96%HEMA (26.8g), and

azobisisobutironitoriru (8.13g) was added to flask 5000ml which has the round bottom of three lots where it was equipped with the nitrogen inlet and overhead mechanical agitation machine which were connected with the thermocouple and desiccation nitrogen supply source which were connected with the organosol capacitor and the digital temperature controller.

[0123] The reaction flask was purged for 30 minutes by the rate of flow of 2 l/min with desiccation nitrogen, agitating the above-mentioned mixture mechanically. Then, the hollow glass plug was inserted in opening of a capacitor, and the nitrogen rate of flow was reduced to about 0.5 l/min. Subsequently, the reaction mixture was heated at 70 degrees C for 16 hours, and the conversion ratio of a product advanced quantitatively by reaction time.

[0124] The above-mentioned mixture was heated to 90 degrees C, it maintained at the temperature for 1 hour, Residual azobisisobutironitoriru was removed, and it adjusted at 70 degrees C. Then, the nitrogen inlet was removed from the reaction flask and DBTDL 13.6g and TMI 41.1g were added to this mixture. It added little by little, having applied TMI in 5 minutes agitating using a stirrer with a magnetic reaction mixture at this time. The hollow glass plug inserted in opening of a capacitor was removed, the nitrogen inlet was connected here, and the interior of a reaction flask was purged for 30 minutes by the rate of flow of about 2 l/min with nitrogen gas. Reinsertion of the hollow glass plug was carried out to opening of a capacitor, and the nitrogen rate of flow was reduced to about 0.5 l/min.

[0125] Subsequently, the conversion ratio of a product was quantitatively obtained by reaction time by making a reaction mixture react at 70 degrees C for 6 hours.

[0126] Then, the above-mentioned reaction mixture was made to cool at a room temperature. A product is an EHMA-HEMA copolymer which has a TMI random surveying chain, and is displayed by EHMA/HEMA-TMI (97/3-4.7% w/w).

[0127] It was used for the above-mentioned copolymer being equipped with the organosol which has 8/1 of a core / shell ratios.

[0128] NORUPA 12 (trade name) (2943g), the above-mentioned copolymer (179.5g, a solid-state content: 26.0%), MMA (93.3g) and EA (280g), and azobisisobutironitoriru (6.3g) mixture were added to the 5000ml round bottom flask of 3 poems with which it was equipped with the nitrogen impregnation tube connected with the thermocouple and desiccation nitrogen supply source which were connected with the overhead mechanical agitation machine, the capacitor, and the digital temperature indicator controller. Said flask was purged for 30 minutes by the rate of flow of about 2 l/min with desiccation nitrogen, agitating a reaction mixture mechanically.

[0129] Then, the rate of flow of nitrogen gas was adjusted at the rate of about 0.5 l/min.

[0130] It heats at 70 degrees C, agitating a reaction mixture, and at this temperature, it maintained for 16 hours and the polymerization was carried out. Then, the reaction mixture was cooled at the room temperature.

[0131] Subsequently, the residual monomer was removed using the revolution evaporator with which it added to the organosol which had about 350g heptane cooled, and dry ice / acetone capacitor was equipped with the obtained mixture, it operated at 95 degrees C, the vacuum was decompressed to about 15 mmHg extent one by one, and the collection rate of a condensate was maintained to the suitable level. The organosol from which the monomer was removed was cooled at the room temperature, and opaque white dispersion liquid were obtained.

[0132] For this organosol, Core Tg (calculated value) is [about]. -It is displayed by EHMA/HEMA-TMI//MMA/EA (97/3-4.7//25/75%w/w) which is 1 degree C.

[0133] Tg (measured value) by DSC (differential scanning calorimeter) was 5.7 degrees C.

[0134] Measuring the solid-state content in the above-mentioned organosol using the describing [above] halogen dry cleaning method, the solid-state content was 20.24% as a result of measurement.

[0135] The liquid toner example (example 1 of comparison) organosol / charge accommodation additive / NORUPA premix (trade name) added Zr HEKISEMU (Hexcem) solution (14.20g, 6.15wt%, OMG Americas Inc.) and NORUPA 12 (trade name) (951.8g) to organosol EHMA/HEMA-TMI//MMA/EA (1034. zero g), and vibrated the above-mentioned mixture for about 30 minutes using the shaker for laboratories. It was used instead of the pigment by which IGARA cisele (Igarashi cell) 0.5L filled up with POTTASU glass bead (Potter's Glass beads) 390g, an organosol / charge modifier / NORUPA premix 294.9g, and unsettled MONAKU 120 (lot [485-732] and Carbot) was processed.

[0136] The constituent was milled for 90 minutes by 2000rpm, and the black ink of 25mg (CCA) content of charge modifiers per 1g of pigments was obtained.

[0137] The particle magnitude and conductivity of black ink were measured by the above-mentioned approach.

[0138] As a result of measurement, the conductivity of 3wt% black ink was 105 pmho/cm, free phase conductivity was 1.42 pmho/cm (free 1.35% phase conductivity), and volume average particle magnitude (Horiba 910) was 0.84 micrometers. Particle magnitude distribution showed the mono-mode in which it had maximum by about 1.20 micrometers. If this toner is used, the printing result it can be satisfied with the reflected light study consistency of 1.49

of a result with thin background development and 500V developer bias will be obtained.

[0139] (Example 1) It is 400ml polyethylene beaker ON **** about a carbon black pigment (20.0g, Monach 120, lot 485-732, and Carbot) and denatured alcohol (60.0g).

[0140] The above-mentioned mixture was made to homogenize for about 3 minutes using the distributed equipment for the poly TRON laboratories (Model #PTs 10/35 and Kinematica), and the viscosity nature paste was obtained. The denatured alcohol solution of Pori (2-vinyl pyridine-course CHIREN) (20.0g, a 2.5wt% solution, Mw = about 220,000 here, although weight average molecular weight is the suitable base, number average molecular weight is used.)) Styrene content: 30%, Aldrich Chemical Company was added to carbon black dispersion liquid.

[0141] The homogenization process was carried out until hypoviscosity black dispersion liquid were obtained. 2. Add 5wt% Pori (2-vinyl pyridine-course CHIREN) 60.0g to dispersion liquid, and carrying out a homogenization process in the condition of having set to No.5 was continued for about 10 minutes.

[0142] The mixed weight ratio of a pigment and a polymer was 10:1. 2600g of deionized water was gradually filled with black dispersion liquid, agitating using the stirrer for laboratories. The pigment dispersion liquid in deionized water were filtered through filtration paper (Whatman #54), and it washed twice by about 150g deionized water.

[0143] The pigment collected according to the above-mentioned process was dried at 50 degrees C for 20 hours, and MONAKU 120 pigment by which Pori (2-vinyl pyridine-course CHIREN) processing was carried out using the mortar for laboratories and the pestle was obtained after that.

[0144] The organosol / charge modifier / NORUPA premix (trade name) added Zr HEKISEMU (Hexcem) solution (14.20g, 6.15wt%, OMG Americas Inc.) and NORUPA 12 (trade name) (951.8g) to organosol EHMA/HEMA-TMI//MMA/EA (1034. zero g), and vibrated the above-mentioned mixture for about 30 minutes using the shaker for laboratories.

[0145] 0. The IGARA cisele of 5L was filled up with POTTASU glass bead 390g, an organosol / charge modifier / NORUPA premix (trade name) 294.9g, and 5.65g of MONAKU 120 pigments by which Pori (2-vinyl pyridine-course CHIREN) processing was carried out. The constituent was milled for 90 minutes by 2000rpm, and the black ink of 25mg (CCA) content of charge modifiers per 1g of pigments was obtained.

[0146] The particle magnitude and conductivity of black ink were measured by the above-mentioned approach.

[0147] As a result of measurement, the conductivity of 3wt% black ink was 185 pmho/cm, free phase conductivity was 9.71 pmho/cm (free 5.2% phase conductivity), and volume average particle magnitude (Horiba910) was 2.56 micrometers. Distribution of particle magnitude showed BAIMODO (bi-modal) (about 30 volume [of a shoulder and a toner] %) which has maximum by about 1.25 micrometers and 4 micrometers. If this toner is used, the printing result it can be satisfied with the reflected light study consistency of 1.44 of a result with 500V developer bias will be obtained.

[0148] The carbon black pigment processed in Pori (2-vinyl pyridine-course CHIREN) is effective for improving the charge organization potency force of a pigment, and conductivity is 135 or more pmhoes, and the ink of a CCA25mg content is obtained from the above-mentioned experimental result per 1g of pigments.

[0149] (Example 2) A carbon black pigment (20.0g, Monach120 and lot 485-732, and Carbot), denatured alcohol (60.0g), and Pori (2-vinyl pyridine-cove chill methacrylate) (about 60g of 2.5wt% solutions, a butyl methacrylate content: 10% and Aldrich Chemical Company) were put into the 400ml polyethylene beaker.

[0150] The above-mentioned reaction mixture was made to homogenize for about 3 minutes using the distributed equipment for the poly TRON laboratories (Model #PTs 10/35 and Kinematica), and carbon black dispersion liquid were obtained. The denatured alcohol solution (100.0g, 2.5wt% denatured alcohol solution) of Pori (2-vinyl pyridine-cove chill methacrylate) was put into these carbon black dispersion liquid.

[0151] Carrying out the homogenization process of the above-mentioned mixture was continued for about 10 minutes in the condition of having set to No.5. The mixed weight ratio of a pigment and a polymer is 5:1.

[0152] Subsequently, 2200g of deionized water was gradually filled with black dispersion liquid, agitating a reaction mixture using the stirrer for laboratories. The pigment dispersion liquid in deionized water were filtered through filtration paper (Whatman #54), and were washed twice by about 150g deionized water.

[0153] The pigment collected according to the above-mentioned process was dried at 50 degrees C for 20 hours, and MONAKU 120 pigment by which Pori (2-vinyl pyridine-cove chill methacrylate) processing was carried out using the mortar for laboratories and the pestle was obtained after that.

[0154] The organosol / charge modifier / NORUPA premix (trade name) added Zr HEKISEMU (Hexcem) solution (14.20g, 6.15wt%, OMG Americas Inc.) and NORUPA 12 (trade name) (951.8g) to organosol EHMA/HEMA-TMI//MMA/EA (1034. zero g), and vibrated the above-mentioned mixture for about 30 minutes using the shaker for laboratories.

[0155] 0. The IGARA cisele of 5L was filled up with POTTASU glass bead 390g, an organosol / charge modifier /

NORUPA premix (trade name) 294.9g, and 6.16g of MONAKU 120 pigments by which Pori (2-vinyl pyridine-cove chill methacrylate) processing was carried out.

[0156] The constituent was milled for 90 minutes by 2000rpm, and the black ink of 25mg (CCA) content of charge modifiers per 1g of pigments was obtained.

[0157] The particle magnitude and conductivity of black ink were measured by the above-mentioned approach.

[0158] As a result of measurement, the conductivity of 3wt% black ink was 233 pmho/cm, free phase conductivity was 11.74 pmho/cm (free 5.0% phase conductivity), and volume average particle magnitude (Horiba910) was 11.0 micrometers. Distribution of particle magnitude showed BAIMODO which has maximum by about 13 micrometers (about 85 wt(s)%) and 1.5 micrometers (about 15 wt(s)%).

[0159] It is effective for the carbon black pigment processed in Pori (2-vinyl pyridine-cove chill methacrylate) raising distribution of toner particle magnitude from the above-mentioned experimental result, and it is effective for making the charge organization potency force of a pigment improve, and conductivity is 135 or more pmhoes, and the ink of a CCA25mg content can be obtained per 1g of pigments.

[0160] (Example 3) The Pori (1-vinyl pyrrolidone-KO-2-dimethylaminoethyl methacrylate) water solution (10.0g of 19wt% water solutions, Mw=1, 000 and 000, and Aldrich Chemical Company) was put into the 400ml beaker, and the polymer solution with which 190g of deionized water which has boiled was added, and the elevated temperature was diluted was obtained. This elevated-temperature solution was added to the carbon black pigment (20.0g, Monach120 and lot 485-732, and Carbot), and this mixture was agitated for 10 minutes using the magnetic stirrer for laboratories. Thus, pass filtration paper (Whatman #5), the obtained slurry was made to filter, and it condensed in volume of about 100ml. At this time, the filtration process of a slurry advanced very late. Moreover, the lump which remains in filtration paper was a black thixotropy gel lump.

[0161] Then, the residue which remains on filtration paper was dried for seven days in the oven adjusted by 50 degrees C, and after carrying out disintegration by hand using a mortar and a pestle, the carbon black pigment by which Pori (1-vinyl pyrrolidone-2-dimethylaminoethyl methacrylate) processing was carried out was obtained.

[0162] An organosol / charge modifier / NORUPA premix (trade name) is Zr HEKISEMU (Hexcem) solution (14.20g, 6.15wt%, OMG Americas Inc.) and trade name NORUPA 12 (951.). 8g was added to organosol EHMA/HEMA-TMI//MMA/EA (1034. zero g), and the above-mentioned mixture was vibrated for about 30 minutes using the shaker for laboratories. 0. The IGARA cisele of 5L was filled up with POTTASU glass bead 390g, an organosol / charge modifier / NORUPA premix (trade name) 294.9g, and 5.14g of MONAKU 120 pigments by which Pori (2-vinyl pyridine-cove chill methacrylate) processing was carried out. The above-mentioned constituent was milled for 90 minutes by 2000rpm, and the black ink of 25mg (CCA) content of charge modifiers per 1g of pigments was obtained.

[0163] The particle magnitude and conductivity of black ink were measured by the above-mentioned approach.

[0164] As a result of measurement, the conductivity of 3wt% black ink was 167 pmho/cm, free phase conductivity was 7.11 pmho/cm (free 4.3% phase conductivity), and volume average particle magnitude (Horiba910) was 5.291 micrometers. Distribution of particle magnitude showed BAIMODO by about 1.3 micrometers (about 40 volume [of a toner] %), and 8.5 micrometers (about 60 volume [of a toner] %). If this toner is used, the printing result it can be satisfied with the reflected light study consistency of 1.29 of a result with the developer bias of 500V will be obtained.

[0165] It is effective for making the charge organization potency force of a pigment improve, and conductivity is 135 or more pmhoes, and the carbon black pigment processed in Pori (1-vinyl pyrrolidone-KO-2-dimethylaminoethyl methacrylate) was able to obtain the ink of 25mgCCA content from the above-mentioned experimental result per 1g of pigments.

[0166] (Example 4) The carbon black pigment (20.0g, Monarch120 and lot 485-732, and Carbot) was added to the Pori (vinyl pyrrolidone-KO-vinyl acetate) solution (100.0g, PVP/VAE-335, the 0.67wt% solution in denatured alcohol, ISP Technologies Inc.).

[0167] The above-mentioned mixture was made to homogenize for about 10 minutes with the distributed equipment for the poly TRON laboratories, and carbon black dispersion liquid were obtained. The mixed weight ratio of a pigment and a polymer was 30:1 in these carbon black dispersion liquid.

[0168] After putting the above-mentioned black dispersion liquid into the aluminum pan and drying this at 80 degrees C for about 20 hours, disintegration was carried out using the mortar for laboratories, and the pestle, and MONAKU 120 pigment by which Pori (vinyl pyrrolidone-KO-vinyl acetate) processing was carried out was obtained.

[0169] The organosol / charge modifier / NORUPA premix (trade name) added Zr HEKISEMU solution (14.20g, 6.15wt%, OMG Americas Inc.) and NORUPA 12 (trade name) (951.8g) to organosol EHMA/HEMA-TMI//MMA/EA (1034. zero g), and vibrated these mixture for about 30 minutes using the shaker for laboratories.

[0170] 0. The IGARA cisele of 5L was filled up with POTTASU glass bead 390g, an organosol / charge modifier /

JORUPA premix (trade name) 294.9g, and 5.31g of MONAKU 120 pigments by which Pori (vinyl pyrrolidone-KO-vinyl acetate) processing was carried out. The black ink of 25mg (CCA) content of charge modifiers per 1g of pigments which mills the above-mentioned constituent for 90 minutes by 2000rpm, and does not have Pori (vinyl pyrrolidone-KO-vinyl acetate) was obtained.

[0171] The particle magnitude and conductivity of black ink were measured by the above-mentioned approach.

[0172] As a result of measurement, the conductivity of 3wt% black ink was 145 pmho/cm, free phase conductivity was 1.77 pmho/cm (free 4.7% phase conductivity), and volume average particle magnitude (Horiba910) was 1.04 micrometers. Distribution of particle magnitude showed the mono-mode.

[0173] It is effective for making the charge organization potency force of a pigment improve, conductivity is 135 or more pmhoes, and the carbon black pigment processed in Pori (vinyl pyrrolidone-KO-vinyl acetate) was able to obtain the ink of a CCA25mg content from the above-mentioned experimental result per 1g of pigments. If the carbon black pigment processed from this example in order to make conductivity improve was used, when milling this under the above-mentioned conditions, not making toner particle magnitude increase compared with an unsettled black pigment will have been recognized.

[0174] (Example 5) Toluene 210g, styrene (Aldrich Chemical Company) 72.0g, dimethylaminoethyl methacrylate (Aldrich Chemical Company), g [28.0] and 2, and 2'-azo-isobutyro-dinitrile (azobisisobutironitoriru, Aldrich Chemical Company) 1.35g was put into the transparent carboy. Thus, the obtained solution was purged for 10 minutes with nitrogen gas, and it was made to arrange in the tumbler with which it was equipped with the ebullition cistern (Lauder-O-meter and Atlas Electric Products) adjusted by 70 degrees C.

[0175] After making it react at 70 degrees C, carrying out the tumbler of the above-mentioned mixture for 16 hours, it took out from the tumbler and was made to cool at a room temperature. Subsequently, they are styrene 72.0g, dimethylaminoethyl methacrylate 28.0g, and azobisisobutironitoriru to a reaction mixture. After adding 1.35g further and purging nitrogen again here, the tumbling was carried out at 70 degrees C for 20 hours. In this way, the precipitate of the opaque viscous liquid gestalt which fills about 3500ml heptane with the toluene solution of the obtained polymer, and has a ***** resemblance paste was obtained. Subsequently, the heptane was moved from the precipitate polymer and the polymer was dried for two days in the oven which has an exhaust port.

[0176] After melting the dried glassiness polymer in toluene, it was made to move and dry like these sediment formation fault twice repeatedly, and styrene / dimethylaminoethyl methacrylate mole ratio (calculated value) obtained the Pori (styrene-KO-dimethylaminoethyl methacrylate) glassiness solid-state product of 8:2.

[0177] Then, the carbon black pigment (20.0g, Monach120 and lot 485-732, and Carbot) was paid to 100g of acetone solutions of 2.0wt% Pori (styrene-KO-dimethylaminoethyl methacrylate).

[0178] The above-mentioned mixture was made to homogenize for about 10 minutes using the distributed equipment for the poly TRON laboratories, and black dispersion liquid were obtained. The mixed weight ratio of a pigment and a polymer was 10:1 in these black dispersion liquid.

[0179] After pouring the above-mentioned black dispersion liquid into 2,600g of deionized water agitated with the stirrer for laboratories gradually, agitating a reaction mixture was continued for 30 minutes. The pigment dispersion liquid in deionized water were filtered through filtration paper (Whatman#54), and it washed twice by about 150g deionized water.

[0180] After drying the pigment collected according to the above-mentioned process at 80 degrees C for 20 hours, MONAKU 120 pigment by which was made to carry out disintegration by hand using the mortar for laboratories and a pestle, and Pori (styrene-KO-dimethylaminoethyl methacrylate) processing was carried out was obtained.

[0181] The organosol / charge modifier / NORUPA premix (trade name) added Zr HEKISEMU solution (14.20g, 6.15wt%, OMG Americas Inc.) and NORUPA 12 (trade name) (951.8g) to organosol EHMA/HEMA-TMI//MMA/EA (1034. zero g), and vibrated these mixture for about 30 minutes using the shaker for laboratories.

[0182] 0. The IGARA cisele of 5L was filled up with POTTASU glass bead 390g, an organosol / charge modifier / NORUPA premix (trade name) 294.9g, and 5.65g of MONAKU 120 pigments by which Pori (styrene-KO-dimethylaminoethyl methacrylate) processing was carried out. The black ink of 25mg (CCA) content of charge modifiers per 1g of pigments which mills the above-mentioned constituent for 90 minutes by 2000rpm, and does not have Pori (styrene-KO-dimethylaminoethyl methacrylate) was obtained.

[0183] The particle magnitude and conductivity of black ink were measured by the above-mentioned approach.

[0184] As a result of measurement, the conductivity of 3wt% black ink was 135 pmho/cm, free phase conductivity was 5.12 pmho/cm (free 3.8% phase conductivity), and volume average particle magnitude (Horiba910) was 0.86 micrometers. Distribution of particle magnitude showed the mono-mode.

[0185] It is effective for making the charge organization potency force of a pigment improve, conductivity is 135 or

nore pmhoes, and the carbon black pigment processed in Pori (styrene-KO-dimethylaminoethyl methacrylate) was able to obtain the ink of a CCA25mg content from the above-mentioned experimental result per 1g of pigments. When milling under the above-mentioned conditions, toner particle magnitude is not made to increase compared with an unsettled black pigment, if the carbon black pigment processed from this example in order to make conductivity improve is used.

[0186] As mentioned above, although the gestalt of the suitable operation concerning this invention was explained, this invention is not limited to this configuration. If it is this contractor, various kinds of examples of correction and examples of modification can be assumed within the limits of the technical thought indicated by the claim, and it will be understood as what is included also about those examples of correction, and the example of modification by the technical range of this invention.

[0187]

[Effect of the Invention] By including the coloring agent by which surface treatment was carried out by the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer, the liquid ink which has the improved charge organization potency force, the conductivity variability which decreased, and the improved distributed stability can be obtained.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the liquid ink containing the color particle by which surface treatment was carried out by the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer, and its manufacture approach. In a detail, more An ink imprint process, an IONO graph, an electrograph, It is related with the liquid ink which has the charge organization potency force which was used for all image formation processes including electrophotography color printing and a PURUFINGU process, and has been improved, the conductivity variability which decreased, and the improved distributed stability, and its manufacture approach.

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PRIOR ART

Description of the Prior Art] Liquid ink is widely used by image formation and presswork, such as offset, bubble jet trademark), an ink jet, sculpture intaglio printing (intaglio), rotogravure printing (rotogravure), electrography, and electrophotography printing. Though the last ink constituent carries out difference of this liquid ink substantially, the pigment dispersion liquid for liquid ink are mostly the same at each process. For example, the stability of the pigment dispersion liquid which are not used under shear strain conditions and high-tension electric field must be independently taken into consideration importantly for the final application of liquid ink.

[0003] Thus, research which an ink presentation can be constituted more freely, and the effectiveness of presswork is raised using this, and reduces the amount of trash by development of the pigment dispersion liquid by which stability has been improved is done continuously.

[0004] In addition, liquid ink says the liquid toner or developer in the electrophotography field containing equipments, such as a photocopy machine, a laser beam printer, and facsimile.

[0005] An electrophotography process includes the phase which forms the static electricity-image latent image on the electrified photo conductor, the phase of contacting liquid development liquid in a photo conductor, and developing an image, and the phase which imprints an image on a television object at the last by irradiating light and exposing the photo conductor generally charged along the direction of an image pattern. The last imprint phase is formed directly or in an indirect through a medium transport member. Generally in response to heat and/or a pressure, melting of the developed image is eternally carried out to a television object.

[0006] A liquid toner contains the insulating liquid which carries out the role of the carrier for dispersion liquid of a charged particle known as a toner particle which generally consists of a coloring agent (for example, a pigment or a color) and a polymer binder. A charge director may contain the liquid development liquid component added in order to adjust the polarity of the charge on a toner particle, and magnitude.

[0007] A liquid toner is divided into two kinds. For convenience, since it is divided into a usual liquid toner and an organosol toner and an organosol toner is [among these] excellent in stability, this is more desirable in the electrophotography field.

[0008] The stable organosol contains the colloidal particle (diameter: 0.1-1 micrometer) of a polymer binder. Generally the above-mentioned particle is compounded by the nonaqueous solubility distribution polymerization with a low dielectric hydrocarbon solvent. He was fastidious, and an organosol particle is adsorbed physically or is stable in three dimensions, without condensing for the activity of a soluble polymer by which the graft was carried out chemically. The most general nonaqueous solubility distribution polymerization method is a free radical polymerization which carries out one or more [of the ethylene partial saturation monomers (for example, an acrylic acid or a methacrylic-acid monomer) dissolved in a hydrocarbon medium] at the time of the polymerization under existence of a prior shaping amphiphilic polymer. A prior shaping amphiphilic polymer is a stabilizer and this consists of two peculiar units. The 1st unit is intrinsically insoluble to a hydrocarbon medium, and the 2nd unit is freely dissolved in a hydrocarbon medium.

[0009] If a monomer converts little by little and reaches critical molecular weight by implementation of the polymerization reaction for manufacturing an organosol particle, it will separate into a precipitate gestalt from a solution across the limitation of the solubility, and a polymer will form a "core" particle. A core is adsorbed, or the amphiphilic polymer forms covalent bond, and by this, a core grows and forms a discrete particle. A particle grows and continues until a monomer is lost, and it enables it to stabilize the amphiphilic polymer "shell" to which the core adhered in three dimensions, without a growth core particle condensing. Thus, as for the formed nonaqueous solubility colloidal dispersion liquid (organosol), a number average diameter contains the core / shell polymer particle of 0.1-0.5-micrometer range.

[0010] Then, the above-mentioned organosol can carry out simple installation of a coloring agent pigment and the charge director, or can mix them, and can make a liquid toner by passing through the processing process by the well-known mixed means effective for contracting particle magnitude by the reduction process or the technical field concerned of high shear homogenization, ball milling, ***** milling, high energy bead (sand) milling, or other particle magnitude at the time of dispersion-liquid formation.

[0011] If mechanical energy is added to dispersion liquid at the time of milling, pigment floc will be made to a primary particle (diameter of 0.05-1.0 micrometers), the role which grinds an organosol to a fragment so that it can adhere to the pigment front face formed newly is carried out, and it is made for the pigment particle stabilized in three dimensions not to condense.

[0012] The electrified nonaqueous solubility pigment dispersion liquid stabilized in three dimensions as a result including the particle which has the number average diameter of 0.1-2.0 micrometers are obtained, and a number average or the weighted mean particle diameter of a toner particle is 0.1-0.5 micrometers in these dispersion liquid. Thus, the dispersion liquid stabilized in three dimensions are suitable for the high resolution print.

[0013] Electrification of liquid ink changes dramatically with pigments. The so-called "charge modifier" and the charge director known are required to adjust an ink conductivity value to an allowed value, and these contents completely change with coloring agent pigments, and are designed by the well-known charge director design principle in ink. The ink containing the coloring agent pigment which is different from each other acts so that it may differ dramatically under the printing conditions of making it expose by high electric field etc. The change based on the electrification property that a coloring agent pigment is different from each other is not desirable. Moreover, although it must be careful about the lot-to-lot variable of a coloring agent pigment, it is because the lot-to-lot variable of a coloring agent pigment causes change which is not desirable in the property of ink. Therefore, it is desirable to have ink which has conductivity and electrical characteristics regardless of the type or lot of a coloring agent pigment.

[0014] Moreover, ink with few charge director contents and the optical density printed when using black ink with a charge director's small content with the current ink constituent especially are reduced, and it is the trouble of exaggerated tones, such as tailing, wash-off, and sludging.

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EFFECT OF THE INVENTION

[Effect of the Invention] By including the coloring agent by which surface treatment was carried out by the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer, the liquid ink which has the improved charge organization potency force, the conductivity variability which decreased, and the improved distributed stability can be obtained.

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TECHNICAL PROBLEM

(The trouble widely recognized to be a side effect with the image formation process) can be reduced. The efforts for for manufacturing efforts, i.e., ink excellent in conductivity, raising the charge organization potency force of ink for effective image formation, even if it reduces a charge director content do not have effectiveness in raising the charge organization potency force, or cause the result which is not desirable as for high free phase conductivity etc. This is defined by the section under toner conductivity and is a well-known property in the liquid electrophotography field.

[0015] The useful charge director of recent years most has the solubility property restricted with the low dielectric constant solvent suitable for electrophotography liquid ink. Consequently, a charge director condenses, as it distributed under the binder of the particle distributed from the liquid, or liquid ink. There is almost no direct physical contact or direct interaction between a coloring agent pigment and a charge director as a result, and an ink imprint is performed in inefficient under the imprint process promoted in static electricity.

[0016] The technique for improving the distributed stability and the charge property of liquid ink is indicated by the following reference.

[0017] The liquid ink containing the block copolymer which has the 1st block which contains the distributed pigment, and a nitrogen content aromatic series vinyl compound and a non-nitrogen aromatic series vinyl compound in the United States patent official report No. 4,665,011, and the 2nd block containing polymerization nature C4-C6 diene is indicated. It is reported that these liquid ink has the outstanding distributed stability and charge stability.

[0018] According to the United States patent official report No. 5,009,980, the thermoplastic binder of an electrification adjuvant is made to distribute substantially insolubility or the aromatic series nitrogen content compound which is not mixed on a nonpolar liquid carrier, and the liquid ink which has the improved image quality is formed.

[0019] According to the United States patent official report No. 4,061,582, poly vinyl acetate is used as a binder and coating is carried out to the front face of a coloring agent pigment particle. The stable liquid ink which has oleophilic [by which the processed pigment particle has improved through the minimum milling process] is produced.

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MEANS

Means for Solving the Problem] In order to solve the above-mentioned technical problem, in the 1st viewpoint of this invention, the liquid ink characterized by including the coloring agent by which surface treatment was carried out by the carrier liquid, the organosol, and the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer is offered.

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MEANS

Means for Solving the Problem] In order to solve the above-mentioned technical problem, in the 1st viewpoint of this invention, the liquid ink characterized by including the coloring agent by which surface treatment was carried out by the carrier liquid, the organosol, and the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer is offered.

[0024] Moreover, in order to solve the above-mentioned technical problem, it sets in the 2nd viewpoint of this invention. The phase which dissolves the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer in a solvent, and forms a polymer solution, (a-1) The phase which distributes a color particle in the above-mentioned polymer solution, and forms coloring agent dispersion liquid, (b-1) (c-1) The manufacture approach of the liquid ink characterized by including the phase which forms the color particle which removed some solvent at least and was processed from the above-mentioned coloring agent dispersion liquid, and the phase of making a carrier liquid content organosol distributing the coloring agent by which processing was carried out [above-mentioned (d-1)] is offered.

[0025] Moreover, in order to solve the above-mentioned technical problem, it sets in the 2nd viewpoint of this invention. The phase which dissolves the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer in a solvent, and forms a polymer solution, (a-2) The phase which distributes a color particle in the above-mentioned polymer solution, and forms coloring agent dispersion liquid, (b-2) (c-2) The manufacture approach of the liquid ink characterized by including the phase of carrying out the sediment of the color particle processed from the above-mentioned coloring agent dispersion liquid, and the phase of making a carrier liquid content organosol distributing the color particle by which processing was carried out [above-mentioned (d-2)] is offered.

[0026] Moreover, as for the nitrogen of the above-mentioned nitrogen content polymerization nature monomer, in the above-mentioned liquid ink and this manufacture approach, it is desirable to exist in the group chosen from the group which consists of an amide (amide), an amide (amido), amino, and an amine group.

[0027] And as for the above-mentioned nitrogen content polymerization nature monomer, it is desirable that it is, or more [it was chosen from the group which consists of the methacrylate which has an aliphatic series amino radical or acrylate, a nitrogen content heterocycle vinyl monomer, the annular amide monomer by which N-vinyl permutation was carried out, an ethylene monomer by which nitrogen radical content aromatic substitution was carried out, and a nitrogen content vinyl ether monomer] one.

[0028] At this time, the methacrylate or acrylate which has the above-mentioned aliphatic series amino radical N and N-dimethylaminoethyl (meta) acrylate, N and N-diethylaminoethyl Acrylate, N, and N-dibutyl aminoethyl (meta) acrylate, N, and N-hydroxyethylamino (meta) acrylate, N-benzyl-N-ethylamino (meta) acrylate, N, and N-dibenzyl aminoethyl (meta) acrylate (Meta) It is, or more [it was chosen from the group which consists of N-octyl, N, and N-dihexyl aminoethyl (meta) acrylate] one. And the above-mentioned nitrogen content heterocycle vinyl monomer N-vinyl imidazole, N-vinyl indazole, N-vinyl tetrazole, 2-vinyl pyridine, 4-vinyl pyridine, a 2-methyl-5-vinyl pyridine, 2-vinyl quinoline, 4-vinyl quinoline, 2-vinyl pyrazine, The annular amide monomer by which is or more [it was chosen from the group which consists of 2-vinyl oxazole and 2-vinyl benzooxazole] one, and N-vinyl permutation was carried out [above-mentioned] The ethylene monomer by which is or more [it was chosen from the group which consists of N vinylpyrrolidone, N-BINIRUPI ** RIDON, and N-vinyl oxazolidone] one, and nitrogen radical content aromatic substitution was carried out [above-mentioned] Dimethylamino styrene, diethylamino styrene, It is, or more [it was chosen from the group which consists of diethylamino methyl styrene and dioctylamino styrene] one. The above-mentioned nitrogen content vinyl ether monomer Vinyl-N-ethyl-N-phenylamino ethyl ether, vinyl-N-butyl-N-phenylamino ethyl ether, triethanolamine divinyl oxide, vinyl diphenylamino ethyl ether, the vinyl pyrrolidyl amino

ether, It is, or more [it was chosen from the group which consists of vinyl-beta-morpholino ethyl ether, an N-vinyl hydroxyethyl benzamide, and m-aminophenyl vinyl ether] one.

[0029] The dispersion liquid obtained from the above (b-1) and (b-2) a phase contain a charge director further. The above-mentioned charge director is the metal salt which consisted of organic anions which are polyvalent metal ion and counter ion. The above-mentioned polyvalent metal ion Ba (II), calcium (II), Mn (II), Zn (II), Zr (IV), Cu (II), aluminum (III), Cr (III), Fe (II), Fe (III), Sb (III), Bi (III), Co (II), La (III), Pb (II), Mg (II), Mo (III) and nickel (II), Ag (I), It is, or more [it was chosen from the group which consists of Sr (II), Sn (IV), V (V), and Y (III) and Ti (IV)] one. The above-mentioned organic anion It is, or more [it was chosen from the group which consists of a sulfonate guided from the carboxylate or aliphatic series sulfonic acid, and aromatic series sulfonic acid which are guided from any one of aliphatic carboxylic acid and aromatic carboxylic acid] one.

[0030] The above (a-1) and (a-2) the Cowley butanol numeric value of the solvent in a phase are 150 30 especially or more 30 or more, and it is desirable that the Cowley butanol numeric value of the above (d-1) and (d-2) the carrier liquid in a phase is 20 to especially less than 30 less than 30.

[0031] Moreover, as for especially the above-mentioned coloring agent, in liquid ink, it is desirable that it is a carbon black pigment.

[0032]

[Embodiment of the Invention] Hereafter, the gestalt of suitable operation of this invention is explained to a detail.

[0033] (Gestalt of the 1st operation) the surface treatment process of the coloring agent concerning this operation gestalt consists of phases of as a result drying an object, after coating a pigment front face, and namely, nitrogen content polymer sediment -- forming -- carrying out the sediment (it is coating about sediment) of the nitrogen content polymer especially under existence of a pigment or processing a coloring agent pigment with a nitrogen content polymer solution, a coloring agent and.

[0034] If the coloring agent pigment by which surface treatment was carried out is used, even if electrification extent improves further and uses a small amount of charge accommodation additive, the liquid ink which has a permissible conductivity value, and the pigment with which the effect of variables, such as a lot and a manufacturer, was reduced in the electrification property will be obtained.

[0035] The liquid ink constituent concerning this operation gestalt contains a carrier liquid, a coloring agent pigment, and an organosol. A coloring agent (especially pigment) is distributed by the mixture of a carrier liquid in this liquid ink constituent.

[0036] A film is formed promptly, without condensing and sedimenting (there being a quick self-process capability), and the ink constituent concerning this operation gestalt is especially useful at the xerography, IONO graph, or static electricity-image formation and other usual presswork.

[0037] As for a carrier fluid, in the above-mentioned ink constituent, it is desirable that it is chosen among well-known various matter by the technical field concerned, and especially the Cowley butanol (KB) numeric value uses less than (less than [Especially / 20 or more] 30) 30 thing. When KB numeric value of a carrier fluid separates from the above-mentioned range, since a graft stabilizer separates from the field which can be dissolved selectively, the role of a stabilizer cannot be played, an ink particle is not formed normally but the dispersibility and stability of an ink particle worsen, it is not desirable.

[0038] KB numeric value -- the ASTM testing method -- although measured by D1133-54T, this measuring method measures the addition tolerance of the hydrocarbon diluent in the 1-butanol solution of the Cowley numeric value of a standard solution. KB numeric value is expressed with the volume (ml) of a 25 degrees C [which is added to 20g of standard Cowley 1-butanol solutions, and can obtain predetermined turbidity] solvent.

[0039] As reference, although an examination value is shown about KB certified value, KB numeric value of toluene is 105 and KB numeric value of the mixture which consists of heptane 75% and toluene 25% is 40.

[0040] Generally the above-mentioned carrier liquid is oleophilic, is stabilized chemically and has insulation. "The liquid which has insulation" means the liquid which has a low dielectric constant and high electrical resistivity here. Dielectric constants are 1-5 five or less, and the dielectric constants of especially this insulating liquid are 1-3 more preferably. At this time, the electrical resistivity of a carrier liquid is more than 109-ohmcm, and is 1010-1016-ohmcm more than 1010-ohmcm especially preferably.

[0041] There is no viscosity comparatively preferably, it is made for a charged particle to move at the time of development, and a carrier liquid can be suitably removed from the substrate with which volatility came out enough and the final image was formed. However, since a carrier liquid has non-volatile, it can minimize loss by a carrier liquid evaporating from a developer. Moreover, a carrier liquid must be inactive chemically to the matter used at a liquid electrophotography process or equipment especially a photo conductor, and its variant front face.

[0042] As a concrete example of a carrier fluid, aliphatic hydrocarbon (n pentane, a hexane, heptane, etc.), alicyclic group hydrocarbons (a cyclopentane, cyclohexane, etc.), aromatic hydrocarbon (benzine, toluene, xylene, etc.), the halogenated hydrocarbon solvents (the chlorinated alkane, the fluorinated alkane, chlorofluorocarbon, etc.), silicone oils, and these mixture can be mentioned. Especially as a carrier fluid, it is desirable that they are branching mold paraffin solvent mixture, such as trade name Isopar G (Isopar G), Isopar H, Isopar K, Isopar L, Isopar M, and Isopar V (Exxon Corporation), and it can mention aliphatic hydrocarbon solvent mixture, such as trade name NORUPA 12, NORUPA 13, and NORUPA 15 (Exxon Corporation), as most desirable carrier fluid.

[0043] A graft stabilizer carries out the role which a core part and a graft reaction are caused [role] and stabilizes an ink particle.

[0044] The constituent of a graft stabilizer is chosen so that the HIRUDE brand solubility variable of a graft stabilizer may approach with the thing of a carrier fluid and may generally become a pair etc., and a stabilizer is dissolved in a carrier solvent and it is fully solvated. Especially as a graft stabilizer, less than 1/2 3.0Mpa(s), if the difference of a carrier liquid comparison HIRUDE brand solubility variable is a 1.0 to less than 1/2 3.0Mpa(s) polymerization nature compound, all have it. [usable] Moreover, if the differences of the effective HIRUDE brand solubility variable of an effective carrier liquid comparison stabilizer are especially less than 1/2 3.0Mpa(s) from 1.0 less than 1/2 3.0Mpa(s), as for a 1/2 or more 3.0Mpa(s) polymerization nature compound, the difference of a carrier fluid comparison HIRUDE brand solubility variable will be used at the time of formation of a copolymer graft stabilizer.

[0045] As for the absolute value difference of the HIRUDE brand solubility variable between a graft stabilizer (shell) and a carrier liquid, it is desirable that it is especially 1/2 2.6 MPas from 2.0.

[0046] As a nonrestrictive example of a useful polymerization nature monomer, at the time of formation of a graft stabilizer 3, 3, 5-trimethyl cyclohexyl methacrylate, hexyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, dodecyl (lauryl) acrylate, octadecyl (stearyl) acrylate, BIHENIRU acrylate, Hexyl methacrylate, 2-ethylhexyl (methacrylate), The indispensable condition of the C6-C30 acrylic acid containing DESHIRU methacrylate, dodecyl (lauryl) methacrylate, octadecyl (stearyl) methacrylate, isobornyl acrylate, and isobornyl methacrylate, methacrylic ester, and the above-mentioned solubility variable There are other acrylate and methacrylate to satisfy.

[0047] It is chemically combined with the resin core (that is, the graft is carried out to the core), or a core is adsorbed and a graft stabilizer remains to the indispensable field of a resin core. Many reactions by which well-known was carried out to this contractor of the technical field concerned are effective for carrying out the graft of the soluble polymer stabilizer to an organosol core at the time of a free radical polymerization.

[0048] Hydroxy ** in which the general graph TINGU approach has a partial saturation nature end group with run DAMUGU rafting of a polyfunctional free radical, the ring opening polymerization of the cyclic ether, ester, an amide, or acetal, and an epoxidation reaction includes the reaction, an esterification reaction (that is, glycidyl methacrylate reacts with a meta-grill acid, and advances the ester reaction under the Miyoshi amine catalyst) and a condensation reaction, or polymerization reaction of an amino chain migration agent.

[0049] As for a graft stabilizer, it is desirable that number average molecular weight is 50,000-1,000,000dalton (Da), and it is 100,000-300,000Da most preferably 100,000 to 500,000 Da. Since a graft stabilizer separates from the field which can be dissolved selectively, and cannot perform the role of a stabilizer, an ink particle is not formed normally but the dispersibility and stability of an ink particle worsen when the number average molecular weight of a graft stabilizer separates from said range, it is not desirable.

[0050] Moreover, the polydispersity of a graft stabilizer affects image formation and the imprint engine performance of a liquid toner. As for especially the polydispersity (ratio of the weight average molecular weight to number average molecular weight) of a graft stabilizer, generally, it is [15 or less / two to less than five] more preferably desirable 1-15, and that it is 2-2.5 most preferably.

[0051] graph TINGU which forms a graph TINGU site -- law introduces a hydroxy group into a graft stabilizer at the time of a free radical polymerization, and makes all or a part of these hydroxy groups react in a consecutive non-free radical reaction phase under ethylene partial saturation nature aliphatic series isocyanate (example: meta-isopropyl dimethylbenzyl isocyanate [TMI]) or 2-SHANATO ethyl methacrylate [IEM], and a catalyst And covalent bond of the graft stabilizer is carried out to the early insoluble acrylic-acid (j) polymer core through the reaction between the partial saturation vinyl group of a graph TINGU site, and an ethylene partial saturation core monomer (example: vinyl ester especially a with a carbon number of less than seven acrylic acid and methacrylic ester or vinyl acetate, vinyl system aromatic compounds, such as styrene, acrylic nitril, n-vinyl pyrrolidone, and vinyl chloride and vinylidene chloride) all over the consecutive free radical polymerization phase.

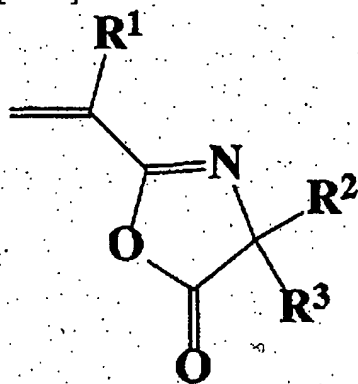
[0052] When making an early insoluble core particle carry out graph TINGU of the prior shaping polymer stabilizer, other effective approaches are already well-known to this contractor of the technique concerned. For example, other

graph TINGU protocols are indicated by the reference of the Barrett dispersion-liquid polymerization (KE.J.Barrett, ed., John Wiley: New York, 1975, section 3.7-3.8, pp 79-106) in an organic medium. An approach especially useful although graph TINGU of the polymer stabilizer is carried out at a core is using a support group.

[0053] The above-mentioned support group offers the share ring of the core section of a particle, and the dissolution component of a solid stabilizer.

[0054] As a monomer including the above-mentioned support group An alkenyl azlactone comonomer, 2-hydroxyethyl methacrylate, 3-hydroxypropyl methacrylate and 2-hydroxyethyl acrylate, a pentaerythritol thoria chestnut rate, 4-hydroxy butyl vinyl ether, The 2-alkenyl -4 which has the addition product and the following structure expression between partial saturation nature nucleophilicity objects including hydroxy , amino or mercaptan groups, such as 9-octadecene-1-ol, cinnamyl alcohol, allyl mercaptan, and meta-allylamine, Azlactones, such as 4-dialkyl azlactone, are suitable.

[0055]



[0056] the inside of the above-mentioned formula, and R1 -- the alkyl group of H or C1-C5 -- desirable -- the alkyl group of C1 -- it is -- R2 and R3 -- the low-grade alkyl group of each C1-C8 -- it is the low-grade alkyl group of C1-C4 preferably.

[0057] A graph TINGU mechanism is ethylene partial saturation nature isocyanate (example: carried out to the hydroxy group which introduced dimethyl-m-isopropanal ** nil benzyl isocyanate (American Cyanamid) into the graft stabilizer precursor (namely, hydroxyethyl methacrylate) before by carrying out graph TINGU.) most preferably.

[0058] A core polymer is performed by INSAICHU by the copolymerization reaction with a stabilizer monomer. forming the ink constituent which the constituent of an insoluble resin core is adjusted preferentially, expresses glass transition temperature (Tg) with a low resin core, and contains resin as a principal component -- the temperature more than the glass Tg of a core -- it is adjusted so that a film may be preferably formed promptly at an elevated temperature from 23 degrees C or this (self-immobilization is made quickly). Quick self-immobilization is a fault at the time of printing (for example, contamination and an imprint imperfect at the time of trailing-edge trailing and high-speed printing are prevented beforehand.). Core Tg has desirable less than 23 degrees C, and less than 10 degrees C is less than -10 degrees C most preferably.

[0059] As a nonrestrictive example of the polymerization nature organic compound suitable for an organosol core Methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, N, and N-dimethylaminoethyl (meta) acrylate, N, and N-diethylaminoethyl Acrylate, N, and N-dibutyl aminoethyl (Meta) Acrylate, M, N-hydroxyethyl aminoethyl (Meta) Acrylate, N-benzyl, N-ethylamino ethyl (Meta) Acrylate, N, and N-dibenzyl aminoethyl (meta) acrylate, N-octyl, N, and N-dihexyl aminoethyl (meta) acrylate, N-vinyl imidazole (N-vinylimidazole), (Meta) N-vinyl indazole, N-vinyl tetrazole, 2-vinyl pyridine, 4-vinyl pyridine, a 2-methyl-5-vinyl pyridine, 2-vinyl quinoline, 4-vinyl quinoline, 2-vinyl pyrazine, 2-vinyl oxazole, 2-vinyl benzoxazole, N-vinylpyrrolidone and N-BINIRUPI ** RIDON, N-vinyl oxazolidone, N-methylacrylamide, N-octyl acrylamide, N-phenyl methacrylamide, N-cyclohexyl acrylamide, Acrylamides (meta), such as N-phenylethyl acrylamide, N-p-methoxy-phenyl acrylamide, acrylamide, N,N-dimethylacrylamide, N, and N-dibutyl acrylamide, N-methyl, and N-phenyl acrylamide PI ** lysine acrylate, morpholine acrylate, Dimethylamino styrene, diethylamino styrene, diethylamino methyl styrene, dioctylamino styrene, vinyl-N-phenylamino ethyl ether, vinyl-N-butyl-N-phenylamino ethyl ether, Triethanolamine divinyl oxide, vinyl diphenylamino ethyl ether, the vinyl pyrrolidyl amino ether, vinyl-beta-morpholino ethyl ether, N-vinyl hydroxyethyl benzamide, m-aminophenyl vinyl ether and other acrylate systems and methacrylate -- there are monomers, such as methyl methacrylate, ethyl acrylate, and dimethylaminoethyl methacrylate, most preferably.

[0060] Although other polymers are independent or it may be used with the above-mentioned matter, he is fastidious and there are a melamine and melamine-formaldehyde-resin, phenol-formaldehyde-resin, epoxy resin, polyester resin, styrene and styrene / acrylic-acid copolymer, vinyl acetate and vinyl acetate / acrylic-acid copolymer, acrylic-acid and methacrylic ester, cellulose acetate, and cellulose acetate-butyrate copolymer and a Pori (vinyl BUCHIRARU) copolymer as a concrete example of a polymer.

[0061] The optimal weight ratio of a resin core and stabilizer shell is 1:1 to 15:1, are 2:1-10:1 preferably, and are 4:1-8:1 most preferably. When a core / shell ratio separates from the above-mentioned range, the effectiveness which is not desirable is acquired. For example, if a core / shell ratio exceeds 15, the graft stabilizer for making it stabilize in three dimensions, without an organosol condensing is inadequate. On the other hand, since the driving force of a polymerization reaction is inadequate with [a core / shell ratio] one [less than], the copolymer solution with which another particle phase which is not organosol dispersion liquid by which shell was stabilized was formed is formed.

[0062] The magnitude of the particle in an organosol does effect like a desiccation process and an imprint fault like the image formation fault of liquid ink. Preferably, it is 0.05-5.0 micrometers, and the magnitude (dynamic light scattering is determined) of the primary particle of an organosol is 0.15-1 micrometer, and is 0.20-0.50 micrometers.

[0063] The liquid ink using the above-mentioned organosol contains the coloring agent contained in thermoplastic organosol resin.

[0064] If it is a coloring agent well-known at the technical field concerned as the above-mentioned coloring agent, all are useful and matter, such as a color, a stain, and a pigment, is included.

[0065] The desirable coloring agent and desirable pigment which are introduced into polymer resin are useful to usually having insolubility and refractoriness to a carrier liquid, and making a latent-image static electricity-image visualize, and effective for it. As a nonrestrictive example of such a coloring agent, a copper phthalocyanine blue (C. I. Pigment Blue 15:1, 15:2, 15:3 and 15:4), Mono-ant RIDOI yellow (C. I. Pigment yellow 1, 3, 65, 73, and 74), FLARIRIDO yellow (C. I. Pigment yellow 12, 13, 14, 17, and 83), Allyl compound amide (Hansa) yellow (C. I. Pigment yellow 10, 97, 105, and 111), Azo red (C. I. Pigment Red 3, 17, 22, 23 and 38, 48:1, 48:2, 52:1, 81 and 179), The Quinacridone Magenta (C. I. Pigment Red 122, 202 and 209), There are black pigments, such as differential-ized carbon (Cabot Monarch 120, Cabot Regal 300R, Cabot Regal 350R, Vulcan X72), etc.

[0066] By the toner particle, the optimal weight ratios of resin and a coloring agent are 1:1-20:1, are 3:1-10:1 preferably, and are 5:1-8:1 most preferably. Generally the content of the total distributed matter in a carrier fluid is 0.5 - 70 % of the weight on the basis of the total liquid development liquid constituent, is 1 - 25 % of the weight preferably, and is 2 - 12 % of the weight most preferably.

[0067] If surface treatment of the coloring agent pigment is carried out using a nitrogen content polymer or a copolymer, it makes the charge organization potency force improve, and can reduce electrification change.

[0068] As a nitrogen content polymer or a copolymer, N and N-dimethylaminoethyl (meta) acrylate, N and N-diethylaminoethyl Acrylate, N, and N-dibutyl aminoethyl (Meta) Acrylate, N, and N-hydroxyethylamino (Meta) (Meta) Aliphatic series amino radicals, such as acrylate, N-benzyl-N-ethylamino (meta) acrylate, N, and N-dibenzyl aminoethyl (meta) acrylate, N-octyl, N, and N-dihexyl aminoethyl (meta) acrylate Have. An acrylate system, N-vinyl imidazole and N-vinyl indazole, N-vinyl tetrazole, 2-vinyl pyridine, 4-vinyl pyridine, a 2-methyl-5-vinyl pyridine, 2-vinyl quinoline, 4-vinyl quinoline, (Meta) Nitrogen content heterocycle vinyl monomers, such as 2-vinyl pyrazine, 2-vinyl oxazole, and 2-vinyl benzoxazole, The annular amide monomer; N-methylacrylamide by which N-vinyl permutation was carried out, such as N vinylpyrrolidone, N-BINIRUPI ** RIDON, and N-vinyl oxazolidone, N-octyl acrylamide, N-phenyl methacrylamide, N-cyclohexyl acrylamide, N-phenylethyl acrylamide, N-p-methoxy-phenyl acrylamide, acrylamide, N,N-dimethylacrylamide, N, and N-dibutyl acrylamide, N-methyl, N-phenyl acrylamide, PI ** lysine acrylate, Morpholine acrylate etc. Acrylate; (Meta) The ethylene monomer containing nitrogen radicals, such as dimethylamino styrene, diethylamino styrene, diethylamino methyl styrene, and dioctylamino styrene, by which aromatic substitution was carried out; Vinyl-N-ethyl-N-phenylamino ethyl ether, Vinyl-N-butyl-N-phenylamino ethyl ether, triethanolamine divinyl oxide, vinyl diphenylamino ethyl ether, the vinyl pyrrolidyl amino ether, vinyl-beta-morpholino ethyl ether, The nitrogen content polymerization nature organic compound chosen from the group which consists of nitrogen content vinyl ether monomers, such as N-vinyl hydroxyethyl benzamide and m-aminophenyl vinyl ether, can be mentioned.

[0069] The above-mentioned polymer must contain at least 1%, at least 2%, at least 5%, at least 8%, at least 10%, or at least 15% of nitrogen content polymerization nature organic compound as mol criteria of a polymerization unit by the polymer containing a nitrogen atom. As for a nitrogen atom, it is desirable that they are a part of an amide (amide), amide (amido), amino, or amine radical, and it is not desirable that they are a part of nitroglycerine or cyano substituent.

[0070] Surface treatment of a coloring agent pigment can be carried out by the general approach well-known as a surface treatment method of a particle by the technical field concerned. As a nonrestrictive example of such a surface-preparation approach, there are the milling or the kneading method, ion penetration method, and flash plate approach of a pigment under solution coating and the drying method, a powder coating method, the approach of carrying out sediment on a pigment front face, a nitrogen content polymer, or copolymer existence.

[0071] Especially a solution coating method is performed when the Cowley butanol numeric value dissolves a nitrogen content polymer or a copolymer in the polar solvent of 30-150 30 or more. As an example of the solvent for a nitrogen content polymer or copolymers, there are a tetrahydrofuran, an acetone, a methyl ethyl ketone, alcohol, water, a methanol, etc. And a coloring agent pigment is added and it is distributed by other well-known means effective in reduction of the particle magnitude in dispersion liquid in high shear mixing, high shear homogenization, ball milling, ***** milling, high energy bead (sand) milling, or the technical field concerned. If mechanical energy is added to dispersion liquid at the time of milling, coloring agent pigment floc can be ground in smaller particle magnitude.

[0072] Then, the coloring agent pigment particle processed by removing a solvent from coloring agent pigment dispersion liquid by the well-known drying method in the technical fields concerned, such as oven, vacuum oven, evaporation, distillation, a spray drying machine, a microwave oven, and an infrared evaporation system, is formed.

[0073] After the Cowley butanol numeric value dissolves a nitrogen content polymer or a copolymer with the polar solvent of 30-150 30 or more, especially the approach of carrying out sediment on a pigment front face adds a coloring agent pigment, and other well-known means effective for reduction of the particle magnitude in dispersion liquid distribute this in high shear mixing, high shear homogenization, ball milling, ***** milling, high energy bead (sand) milling, or the technical field concerned. And a non-solvent is added and the front face of a coloring agent pigment is coated with sediment of a nitrogen content polymer or a copolymer.

[0074] All can be used for a non-solvent if a nitrogen content polymer is the liquid seldom dissolved. A non-solvent is chosen by a polar solvent and a nitrogen content polymer, or the copolymer.

[0075] A flash plate approach is kneaded or mixed with the resin solution in the condition that the water which covers each pigment particle front face was permuted by the resin solution, in water-soluble pigment dispersion liquid. This pigment sample by which flash plate processing was carried out is usable as dispersion liquid in drying. The above-mentioned resin concerning this operation gestalt is a nitrogen content polymer or a copolymer.

[0076] It will be as follows if the two typical manufacture approaches of the liquid ink concerning this operation gestalt are investigated with reference to the surface treatment approach of the above-mentioned coloring agent pigment.

[0077] The 1st manufacture approach is the thing of an about when especially the front face of a pigment is processed with the above-mentioned solution coating method, a coloring agent and.

[0078] First, the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer is dissolved in a solvent, and a polymer solution is formed. Subsequently, a coloring agent pigment particle is distributed in the above-mentioned polymer solution, and coloring agent pigment dispersion liquid are formed.

[0079] Then, the coloring agent pigment particle which removed some solvent at least and was processed from the above-mentioned coloring agent pigment dispersion liquid is formed, and the liquid ink concerning this operation gestalt is completed by making a carrier liquid content organosol distribute the coloring agent pigment particle by which surface treatment was carried out in this way.

[0080] The 2nd manufacture approach is enforced by the approach of carrying out the sediment of the polymer containing the unit guided to the above-mentioned pigment front face from at least one nitrogen content polymerization nature monomer at the time of the surface treatment of a coloring agent (especially pigment).

[0081] First, the polymer containing the unit guided from at least one nitrogen content polymerization nature monomer is dissolved in a solvent, a polymer solution is formed, a coloring agent pigment particle is distributed in the above-mentioned polymer solution, and coloring agent pigment dispersion liquid are formed.

[0082] The liquid ink concerning this operation gestalt is completed by settling the coloring agent pigment particle processed from the coloring agent pigment dispersion liquid formed of the above-mentioned process, and making a carrier liquid content organosol distribute the color particle by which processing was carried out [above-mentioned].

[0083] On the other hand, an electrophotography liquid toner introduces a charge modifier into liquid ink, and makes it. The charge modifier known as the so-called "charge director" provides a toner particle with a uniform charge polarity.

[0084] A charge director is introduced into a toner particle by the approach with various approaches of chelating to functional groups, such as an approach to which a toner particle is made reacting chemically with a charge director, a method of making a toner particle adsorbing a charge director physically or a stabilization group, an antioxidation nature group, and a charge refining group, approaches of introducing solubility, undissolved, or an emulsifiability group into a toner particle, etc. A desirable approach is making a graft stabilizer using a functional group. A charge

director plays the role which gives the charge of a predetermined polarity of a toner particle, and all are usable if he is a charge director in the technical field concerned. For example, a charge director can introduce into the gestalt of the metal salt which consisted of organic anions as polyvalent metal ion and counter ion.

[0085] As the above-mentioned metal ion, Ba (II), calcium (II), Mn (II), Zn (II), Zr (IV), Cu (II), aluminum (III), Cr (III), Fe (II), Fe (III), Sb (III), Bi (III), Co (II), La (III) and Pb (II), Mg (II), Mo (III), nickel (II), Ag (I), Sr (II), Sn (IV), V (V), Y (III), Ti (IV), etc. are suitable. As the above-mentioned organic anion Aliphatic series or the carboxylate guided from aromatic carboxylic acid or a sulfonic acid or a sulfonate -- there are aliphatic series fatty acids, such as stearin acid, behenic acid, a neo decanoic acid, diisopropyl salicylic acid, an octanoic acid, an abietic acid, a naphthenic acid, a lauric acid, and the Tallinn acid, preferably.

[0086] the metal carboxylate (soap) indicated by the U.S. Pat. No. 3,411,936 number as reference in this operation gestalt as a desirable positive charge director -- it is -- this -- at least -- the alkaline earth metals of the fatty acid of a carbon number 6-7 and a heavy-metal salt, and naphthenic-acid content ring aliphatic series **** -- it is polyvalent metal soap of a zirconium and aluminum more preferably, and is zirconium soap (Zirconium HEX-CEM and Mooney Chemicals) of an octanone acid most preferably.

[0087] The desirable charge direction level used for a toner constituent changes with many factors containing the ratio of reclamation of a graft stabilizer and an organosol, the molecular weight of an organosol, the particle magnitude of an organosol, the core / shell ratio of a graft stabilizer, the pigment for toner manufacture, and an organosol and a pigment. Moreover, desirable charge direction level changes with designs of the essence like an electrophotography image formation fault especially development hardware, and a photosensitive element. However, if it is this contractor of the technical field concerned, it will adjust so that the result which asks for the level of the charge direction based on the above-mentioned variable in each application can be obtained.

[0088] The conductivity of a liquid toner is clearly established by the efficiency metrics of the toner in an electrophotography image by the technical field concerned. In addition, the useful conductivity range is 1.0×10^{-11} - 10.0×10^{-11} mho/cm.

[0089] That the conductivity of a liquid toner is high means things, if a charge forms a crowd on a toner particle at imperfection. This is understood from the relation between current density and the toner accumulated at the time of development not being not much close.

[0090] On the other hand, the toner particle is not charged or that the conductivity of a liquid toner is low means that there is almost nothing. This causes a very low development rate.

[0091] Generally it is well-known to use a charge director compound so that electrification of each particle may fully be performed. In recent years, the data that many unnecessary charges located in the electrification kind of the liquid in a carrier fluid existed became clear in the approach of using a charge director. Thus, an unnecessary charge makes development inefficient-wise, instability-wise, and in being un-consistent.

[0092] In this operation gestalt, the charge was made to exist locally on a toner particle, it prevented substantially that a charge moved to a liquid from this particle, and the above-mentioned trouble has been substantially improved greatly by [it is made for other unnecessary charge components not to exist in a liquid] endeavoring.

[0093] As criteria of the property demanded, these researchers use the ratio of the conductivity of the carrier liquid shown with a liquid toner, and the conductivity (toner dispersion liquid constituted thoroughly) of a general liquid toner. this ratio -- less than 0.6 -- especially -- 0.01 to 0.6 -- desirable -- 0.01 to 0.4 -- and it is 0.01-0.3 most preferably. Other above-mentioned conventional toners have a larger ratio than this in the 0.95 range.

[0094] Various approaches are used for reducing the particle magnitude of a pigment at the time of manufacture of a gel liquid toner. The approach which used other well-known means as a suitable approach by high shear homogenization, ball milling, ***** milling, high energy bead (sand) milling, or the technical field concerned is mentioned.

[0095] Generally by the xerography, the static electricity-image (1) photosensitivity element One or more phases are minded for the phase of electrifying homogeneity in applied voltage, the phase which some (2) photosensitivity elements are exposed and electrified with a radiation supply source, and forms a latent-image image, the phase which adds (3) toners to a latent-image image, and forms a hue image, and (4) hue image. A photosensitive element is formed on the sheet by which coating was carried out, a drum, or a belt by passing through the phase imprinted on the last television object sheet. As for a hue image, for other applications, it is desirable to make it fix at the heated pressure roller or the technical field concerned using other well-known fixed approaches.

[0096] One static electricity-charge is positive charge or a negative charge among a toner particle or a photosensitive element, and the electrophotography process in this operation gestalt is performed by distributing a charge on the photosensitive element preferably charged with positive charge.

[0097] Furthermore, the toner charged with positive charge joins the field to which positive charge was distributed using the liquid toner charge development technique. This development process is performed by the uniform electric field formed with the development electrode located near the photosensitive element front face. Bias voltage is impressed to an electrode in the medium magnitude of an initial electrification surface electrical potential difference and an exposure surface voltage level.

[0098] An electrical potential difference is adjusted so that the tone playback scale for halftone dots can be obtained without the maximum consistency level demanded and the background accumulated.

[0099] A liquid toner flows between an electrode and photosensitive elements. The electrified toner particle is fluid at electric field, and it adheres to it to the electrification field of a photosensitive element, and does not adhere to it in the field in which a non-charged image is not formed. The liquid toner of the excess amount which remains to a photosensitive element is removed by the well-known approach by the technical field concerned. Then, it is made to dry or a photosensitive element front face is made to be dried under room temperature conditions.

[0100] Two variables estimate the quality of liquid ink.

(1) Conductivity (2) which is ink Stability of ink with time [0101] The ink concerning this operation gestalt has little conductivity change by this, when it excels in conductivity on low current director level and a coloring agent pigment is changed. The ink concerning especially this operation gestalt forms a high resolution and high-speed multi-color image, when it is combined with a reversal double layer photo conductor and used at a liquid charge development electrophotography process.

[0102] Its all are usable if the substrate which televises an image from a photosensitive element is the common television object matter like paper, coating paper, a polymer film, and the first stage or the polymer film by which coating was carried out. Moreover, the front face covered with the metal or metal which coating was specially carried out or was processed is usable as a television object. A polymer film contains the plasticized poly vinyl chloride (PVC) which was reached and blended, an acrylic-acid system, a polyurethane system, polyethylene / acrylic-acid copolymer, and poly vinyl BUCHIRARU. Moreover, an available composite is commercially [Scotchcal, Scotchlite, Panaflex (trade name), etc.] useful at the time of substrate manufacture.

[0103] The process in which a final television object or an imprint medium is made to imprint the image formed from the electrification front face introduces the variant promoting agent in the particulate material used in order to form an image, and improves. If the silicon content matter or the fluorine content matter is introduced into the external (shell) layer of a particle, the effective imprint of an image will be promoted.

[0104] It sets like a multicolor image formation fault, and the sequence is not restricted specially but a toner joins the front face of a dielectric element or a photosensitive element. However, it is desirable to take into consideration the point that reversal takes place, and to add an image in special sequence with the transparency and reinforcement of a color for a coloring-reason, at the time of an imprint. For example, the sequence that a more direct image formation fault is as desirable as a double imprint fault is the order of yellow, a Magenta, cyanogen, and black. Moreover, desirable sequence is the order of black, cyanogen, a Magenta, and yellow at a single imprint process. In order that yellow may generally avoid the contamination from other toners, an image is formed first, and since a black toner generally acts as a filter of an exposure supply source, finally black forms an image.

[0105] The conductivity value for using liquid ink most efficiently is 50-1200pico. It is the range of mho-cm -1 . The liquid ink manufactured by the approach concerning this operation gestalt is 500 from the case of the dispersion liquid which contain % of the weight of a solid-state 2.5%, 100 [for example,],pico. It is mho-cm -1 .

[0106] Selectively, the process which carries out over coating of the imprint image carries out an image in order to protect physical breakage and/or chemical-rays breakage. The over coating constituent is well-known at the technical field concerned, and contains the polymer for polymer film formation which was generally dissolved in the volatile solvent or floated. An ultraviolet-rays optical absorption agent may be selectively added to the above-mentioned coating constituent. Moreover, the approach of carrying out the lamination of the image protective layer to the front face in which the image was formed is well-known at the technical field concerned, and the approach of starting is used in this operation gestalt.

[0107] Hereafter, the example concerning this invention is explained. In addition, this invention is not limited to this example.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
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EXAMPLE

[Example] A chemistry abbreviation and the glossary following raw material of a chemical source are used for the polymer manufacture approach of this example.

[0109] The catalysts used by this example are azobisisobutyronitril (trade name VAZO-64 which came to hand from azobisisobutyronitril and DuPont Chemical), and dibutyltin dilaurate (Dibutyl Tin Dilaurate) (DBTDL, Aldrich Chemical Co.). A monomer is Scientific unless reference is made specially. Polymer It is available from Product and Inc.

[0110] The monomer of this example is displayed in the following abbreviation.

[0111] dimethyl-m-isopropanal ** nil benzyl isocyanate (TMI and CYTEC Industries); -- ethyl acetate (EA); 2-ethylhexyl methacrylate (EHMA); -- 2-hydroxyethyl methacrylate (HEMA); and methyl methacrylate (MMA)

[0112] The analysis test approach following test approach is used in order to evaluate the polymer in this operation gestalt, and the property of ink.

[0113] The solid-state content in a graft stabilizer, an organosol and the solid-state content graft stabilizer solution in a liquid toner, an organosol, and ink dispersion liquid carried out gravimetric analysis using halogen lamp desiccation oven with a precision analysis balance (Mettler Instruments Inc.). The solid-state content was respectively measured by about 2g sample using the sample dry down method.

[0114] Various properties of a graft stabilizer molecular weight graft stabilizer are important for the engine performance of the stabilizer containing molecular weight and molecular weight polydispersity. Generally graft stabilizer molecular weight is displayed with weight average molecular weight (Mw), and molecular weight polydispersity is displayed by the ratio (Mw/Mn) of weight average molecular weight and number average molecular weight. Although the molecular weight variable of a graft stabilizer is determined by gel permeation chromatography (GPC), as a carrier solvent, a tetrahydrofuran is used at this time. Absolutely, Mw was determined by the Dawn DSP-F light-scattering detector (Dawn DSP-Flight scattering detector) (Wyatt Technology Corp.), and the rate of a part for Mn measurement and Mw measured value estimated polydispersity using the OPUCHIRABU (optilab) 903 differential-refractometer detector.

[0115] Liquid toner property In order to evaluate the property of a liquid toner, physical and direct assessment of the image quality acquired by measuring chemical property and developing a toner by the LEP image formation mechanism of a toner is required.

[0116] The measured toner property can be divided roughly into a magnitude related characteristic (particle magnitude) and an electrification related characteristic (bulk and free phase conductivity, dynamic mobility, and F-potential).

[0117] Distribution of particle magnitude toner particle magnitude was measured using the analyzer (Horiba LA-900 laser diffraction particle size analyzer) (Horiba Instruments, Inc.) of Horiba LA-900 laser diffraction particle magnitude. The toner sample was diluted with about 1/500 volume ratio, and was ultrasonicated for 1 minute by 150W and 20kHz before measurement. Toner particle magnitude is expressed with the number average base so that the role of the directions person of the basic (primary) particle magnitude of an ink particle may be performed.

[0118] Toner conductivity liquid toner conductivity (bulk conductivity, kb) was measured by about 18Hz using SAIENTIFIKA model 627 conductometry equipment (Scientifica model 6277 conductivity meter) (Scientifica Instruments, Inc.). Moreover, free (dispersant) phase conductivity (kf) was measured without the toner particle. The toner particle was made to separate from a liquid environment by carrying out centrifugal separation at 6,000rpm (6,110 relative centrifugal force) and 5 degrees C with a Joan (Jouan) MR1822 centrifugal-separation vessel (Winchester, VA) for 1 to 2 hours.

[0119] The floating liquid was moved carefully and the conductivity of this liquid was measured using SAIENTIFIKA model 627 conductometry equipment. The free phase conductivity percent to bulk toner conductivity was measured at

100% (kf/kb).

[0120] Particle mobility toner particle electrophoretic mobility (dynamic mobility) was measured using the MATEKKU MBS-8000 **** supersonic-wave amplitude analysis apparatus (Matec MBS-8000 Electrokinetics Sonic Amplitude Analyzer; Matec Applied Sciences, Inc.). Unlike the electrokinetics measurement based on detailed electrical-and-electric-equipment migration, MBS-8000 analysis apparatus has the advantage that it is not necessary to dilute the toner sample for acquiring a mobility value. Therefore, the dynamic mobility of a toner particle can be actually measured by desirable solid-state concentration at the time of printing.

[0121] MBS-8000 analysis apparatus measures the reaction of the charged particle in high-frequency (1.2MHz) alternating current (AC) electric field. At high-frequency AC electric field, a supersonic wave arises on the same frequency of impression electric field by relative migration between an electrification toner particle and the surrounding quality of a dispersion medium (counter ion content). It is measurable in the amplitude of a 1.2MHz supersonic wave using a piezoelectric quartz converter. This **** supersonic-wave amplitude (ESA) is in direct proportion to the low electric-field AC electrical-and-electric-equipment mobility of a particle. Furthermore, particle F-potential is calculable with the above-mentioned equipment from dynamic mobility measured value and well-known toner particle magnitude, dispersant liquid viscosity, and a liquid dielectric constant.

[0122] The mixture of NORUPA 12 (trade name) (2561g), EHMA (849g), 96%HEMA (26.8g), and azobisisobutironitoriru (8.13g) was added to flask 5000ml which has the round bottom of three lots where it was equipped with the nitrogen inlet and overhead mechanical agitation machine which were connected with the thermocouple and desiccation nitrogen supply source which were connected with the organosol capacitor and the digital temperature controller.

[0123] The reaction flask was purged for 30 minutes by the rate of flow of 2 l/min with desiccation nitrogen, agitating the above-mentioned mixture mechanically. Then, the hollow glass plug was inserted in opening of a capacitor, and the nitrogen rate of flow was reduced to about 0.5 l/min. Subsequently, the reaction mixture was heated at 70 degrees C for 16 hours, and the conversion ratio of a product advanced quantitatively by reaction time.

[0124] The above-mentioned mixture was heated to 90 degrees C, it maintained at the temperature for 1 hour, Residual azobisisobutironitoriru was removed, and it adjusted at 70 degrees C. Then, the nitrogen inlet was removed from the reaction flask and DBTDL 13.6g and TMI 41.1g were added to this mixture. It added little by little, having applied TMI in 5 minutes agitating using a stirrer with a magnetic reaction mixture at this time. The hollow glass plug inserted in opening of a capacitor was removed, the nitrogen inlet was connected here, and the interior of a reaction flask was purged for 30 minutes by the rate of flow of about 2 l/min with nitrogen gas. Reinsertion of the hollow glass plug was carried out to opening of a capacitor, and the nitrogen rate of flow was reduced to about 0.5 l/min.

[0125] Subsequently, the conversion ratio of a product was quantitatively obtained by reaction time by making a reaction mixture react at 70 degrees C for 6 hours.

[0126] Then, the above-mentioned reaction mixture was made to cool at a room temperature. A product is an EHMA-HEMA copolymer which has a TMI random surveying chain, and is displayed by EHMA/HEMA-TMI (97/3-4.7% w/w).

[0127] It was used for the above-mentioned copolymer being equipped with the organosol which has 8/1 of a core / shell ratios.

[0128] NORUPA 12 (trade name) (2943g), the above-mentioned copolymer (179.5g, a solid-state content: 26.0%), MMA (93.3g) and EA (280g), and azobisisobutironitoriru (6.3g) mixture were added to the 5000ml round bottom flask of 3 poems with which it was equipped with the nitrogen impregnation tube connected with the thermocouple and desiccation nitrogen supply source which were connected with the overhead mechanical agitation machine, the capacitor, and the digital temperature indicator controller. Said flask was purged for 30 minutes by the rate of flow of about 2 l/min with desiccation nitrogen, agitating a reaction mixture mechanically.

[0129] Then, the rate of flow of nitrogen gas was adjusted at the rate of about 0.5 l/min.

[0130] It heats at 70 degrees C, agitating a reaction mixture, and at this temperature, it maintained for 16 hours and the polymerization was carried out. Then, the reaction mixture was cooled at the room temperature.

[0131] Subsequently, the residual monomer was removed using the revolution evaporator with which it added to the organosol which had about 350g heptane cooled, and dry ice / acetone capacitor was equipped with the obtained mixture, it operated at 95 degrees C, the vacuum was decompressed to about 15 mmHg extent one by one, and the collection rate of a condensate was maintained to the suitable level. The organosol from which the monomer was removed was cooled at the room temperature, and opaque white dispersion liquid were obtained.

[0132] For this organosol, Core Tg (calculated value) is [about]. -It is displayed by EHMA/HEMA-TMI///MMA/EA (97/3-4.7//25/75%w/w) which is 1 degree C.

0133] Tg (measured value) by DSC (differential scanning calorimeter) was 5.7 degrees C.

0134] Measuring the solid-state content in the above-mentioned organosol using the describing [above] halogen dry leaning method, the solid-state content was 20.24% as a result of measurement.

0135] The liquid toner example (example 1 of comparison) organosol / charge accommodation additive / NORUPA remix (trade name) added Zr HEKISEMU (Hexcem) solution (14.20g, 6.15wt%, OMG Americas Inc.) and NORUPA 2 (trade name) (951.8g) to organosol EHMA/HEMA-TMI//MMA/EA (1034. zero g), and vibrated the above-mentioned mixture for about 30 minutes using the shaker for laboratories. It was used instead of the pigment by which GARA cisele (Igarashi cell) 0.5L filled up with POTTASU glass bead (Potter's Glass beads) 390g, an organosol / charge modifier / NORUPA premix 294.9g, and unsettled MONAKU 120 (lot [485-732] and Carbot) was processed.

0136] The constituent was milled for 90 minutes by 2000rpm, and the black ink of 25mg (CCA) content of charge modifiers per 1g of pigments was obtained.

0137] The particle magnitude and conductivity of black ink were measured by the above-mentioned approach.

0138] As a result of measurement, the conductivity of 3wt% black ink was 105 pmho/cm, free phase conductivity was .42 pmho/cm (free 1.35% phase conductivity), and volume average particle magnitude (Horiba 910) was 0.84 micrometers. Particle magnitude distribution showed the mono-mode in which it had maximum by about 1.20 micrometers. If this toner is used, the printing result it can be satisfied with the reflected light study consistency of 1.49 of a result with thin background development and 500V developer bias will be obtained.

0139] (Example 1) It is 400ml polyethylene beaker ON **** about a carbon black pigment (20.0g, Monach 120, lot 185-732, and Carbot) and denatured alcohol (60.0g).

0140] The above-mentioned mixture was made to homogenize for about 3 minutes using the distributed equipment for the poly TRON laboratories (Model #PTs 10/35 and Kinematica), and the viscosity nature paste was obtained. The denatured alcohol solution of Pori (2-vinyl pyridine-course CHIREN) (20.0g, a 2.5wt% solution, Mw = about 220,000 here, although weight average molecular weight is the suitable base, number average molecular weight is used.)) Styrene content: 30%, Aldrich Chemical Company was added to carbon black dispersion liquid.

0141] The homogenization process was carried out until hypoviscosity black dispersion liquid were obtained. 2. Add 5wt% Pori (2-vinyl pyridine-course CHIREN) 60.0g to dispersion liquid, and carrying out a homogenization process in the condition of having set to No.5 was continued for about 10 minutes.

0142] The mixed weight ratio of a pigment and a polymer was 10:1. 2600g of deionized water was gradually filled with black dispersion liquid, agitating using the stirrer for laboratories. The pigment dispersion liquid in deionized water were filtered through filtration paper (Whatman #54), and it washed twice by about 150g deionized water.

0143] The pigment collected according to the above-mentioned process was dried at 50 degrees C for 20 hours, and MONAKU 120 pigment by which Pori (2-vinyl pyridine-course CHIREN) processing was carried out using the mortar for laboratories and the pestle was obtained after that.

0144] The organosol / charge modifier / NORUPA premix (trade name) added Zr HEKISEMU (Hexcem) solution (14.20g, 6.15wt%, OMG Americas Inc.) and NORUPA 12 (trade name) (951.8g) to organosol EHMA/HEMA-TMI//MMA/EA (1034. zero g), and vibrated the above-mentioned mixture for about 30 minutes using the shaker for laboratories.

0145] 0. The IGARA cisele of 5L was filled up with POTTASU glass bead 390g, an organosol / charge modifier / NORUPA premix (trade name) 294.9g, and 5.65g of MONAKU 120 pigments by which Pori (2-vinyl pyridine-course CHIREN) processing was carried out. The constituent was milled for 90 minutes by 2000rpm, and the black ink of 25mg (CCA) content of charge modifiers per 1g of pigments was obtained.

0146] The particle magnitude and conductivity of black ink were measured by the above-mentioned approach.

0147] As a result of measurement, the conductivity of 3wt% black ink was 185 pmho/cm, free phase conductivity was 9.71 pmho/cm (free 5.2% phase conductivity), and volume average particle magnitude (Horiba910) was 2.56 micrometers. Distribution of particle magnitude showed BAIMODO (bi-modal) (about 30 volume [of a shoulder and a toner] %) which has maximum by about 1.25 micrometers and 4 micrometers. If this toner is used, the printing result it can be satisfied with the reflected light study consistency of 1.44 of a result with 500V developer bias will be obtained.

0148] The carbon black pigment processed in Pori (2-vinyl pyridine-course CHIREN) is effective for improving the charge organization potency force of a pigment, and conductivity is 135 or more pmhoes, and the ink of a CCA25mg content is obtained from the above-mentioned experimental result per 1g of pigments.

0149] (Example 2) A carbon black pigment (20.0g, Monach120 and lot 485-732, and Carbot), denatured alcohol (60.0g), and Pori (2-vinyl pyridine-cove chill methacrylate) (about 60g of 2.5wt% solutions, a butyl methacrylate content: 10% and Aldrich Chemical Company) were put into the 400ml polyethylene beaker.

0150] The above-mentioned reaction mixture was made to homogenize for about 3 minutes using the distributed

equipment for the poly TRON laboratories (Model #PTs 10/35 and Kinematica), and carbon black dispersion liquid were obtained. The denatured alcohol solution (100.0g, 2.5wt% denatured alcohol solution) of Pori (2-vinyl pyridine-cove chill methacrylate) was put into these carbon black dispersion liquid.

[0151] Carrying out the homogenization process of the above-mentioned mixture was continued for about 10 minutes in the condition of having set to No.5. The mixed weight ratio of a pigment and a polymer is 5:1.

[0152] Subsequently, 2200g of deionized water was gradually filled with black dispersion liquid, agitating a reaction mixture using the stirrer for laboratories. The pigment dispersion liquid in deionized water were filtered through filtration paper (Whatman #54), and were washed twice by about 150g deionized water.

[0153] The pigment collected according to the above-mentioned process was dried at 50 degrees C for 20 hours, and MONAKU 120 pigment by which Pori (2-vinyl pyridine-cove chill methacrylate) processing was carried out using the mortar for laboratories and the pestle was obtained after that.

[0154] The organosol / charge modifier / NORUPA premix (trade name) added Zr HEKISEMU (Hexcem) solution (14.20g, 6.15wt%, OMG Americas Inc.) and NORUPA 12 (trade name) (951.8g) to organosol EHMA/HEMA-TMI//MMA/EA (1034. zero g), and vibrated the above-mentioned mixture for about 30 minutes using the shaker for laboratories.

[0155] 0. The IGARA cisele of 5L was filled up with POTTASU glass bead 390g, an organosol / charge modifier / NORUPA premix (trade name) 294.9g, and 6.16g of MONAKU 120 pigments by which Pori (2-vinyl pyridine-cove chill methacrylate) processing was carried out.

[0156] The constituent was milled for 90 minutes by 2000rpm, and the black ink of 25mg (CCA) content of charge modifiers per 1g of pigments was obtained.

[0157] The particle magnitude and conductivity of black ink were measured by the above-mentioned approach.

[0158] As a result of measurement, the conductivity of 3wt% black ink was 233 pmho/cm, free phase conductivity was 11.74 pmho/cm (free 5.0% phase conductivity), and volume average particle magnitude (Horiba910) was 11.0 micrometers. Distribution of particle magnitude showed BAIMODO which has maximum by about 13 micrometers (about 85 wt(s)%) and 1.5 micrometers (about 15 wt(s)%).

[0159] It is effective for the carbon black pigment processed in Pori (2-vinyl pyridine-cove chill methacrylate) raising distribution of toner particle magnitude from the above-mentioned experimental result, and it is effective for making the charge organization potency force of a pigment improve, and conductivity is 135 or more pmhoes, and the ink of a CCA25mg content can be obtained per 1g of pigments.

[0160] (Example 3) The Pori (1-vinyl pyrrolidone-KO-2-dimethylaminoethyl methacrylate) water solution (10.0g of 19wt% water solutions, Mw=1, 000 and 000, and Aldrich Chemical Company) was put into the 400ml beaker, and the polymer solution with which 190g of deionized water which has boiled was added, and the elevated temperature was diluted was obtained. This elevated-temperature solution was added to the carbon black pigment (20.0g, Monach120 and lot 485-732, and Carbot), and this mixture was agitated for 10 minutes using the magnetic stirrer for laboratories. Thus, pass filtration paper (Whatman #5), the obtained slurry was made to filter, and it condensed in volume of about 100ml. At this time, the filtration process of a slurry advanced very late. Moreover, the lump which remains in filtration paper was a black thixotropy gel lump.

[0161] Then, the residue which remains on filtration paper was dried for seven days in the oven adjusted by 50 degrees C, and after carrying out disintegration by hand using a mortar and a pestle, the carbon black pigment by which Pori (1-vinyl pyrrolidone-2-dimethylaminoethyl methacrylate) processing was carried out was obtained.

[0162] An organosol / charge modifier / NORUPA premix (trade name) is Zr HEKISEMU (Hexcem) solution (14.20g, 6.15wt%, OMG Americas Inc.) and trade name NORUPA 12 (951.). 8g was added to organosol EHMA/HEMA-TMI//MMA/EA (1034. zero g), and the above-mentioned mixture was vibrated for about 30 minutes using the shaker for laboratories. 0. The IGARA cisele of 5L was filled up with POTTASU glass bead 390g, an organosol / charge modifier / NORUPA premix (trade name) 294.9g, and 5.14g of MONAKU 120 pigments by which Pori (2-vinyl pyridine-cove chill methacrylate) processing was carried out. The above-mentioned constituent was milled for 90 minutes by 2000rpm, and the black ink of 25mg (CCA) content of charge modifiers per 1g of pigments was obtained.

[0163] The particle magnitude and conductivity of black ink were measured by the above-mentioned approach.

[0164] As a result of measurement, the conductivity of 3wt% black ink was 167 pmho/cm, free phase conductivity was 7.11 pmho/cm (free 4.3% phase conductivity), and volume average particle magnitude (Horiba910) was 5.291 micrometers. Distribution of particle magnitude showed BAIMODO by about 1.3 micrometers (about 40 volume [of a toner] %), and 8.5 micrometers (about 60 volume [of a toner] %). If this toner is used, the printing result it can be satisfied with the reflected light study consistency of 1.29 of a result with the developer bias of 500V will be obtained.

[0165] It is effective for making the charge organization potency force of a pigment improve, and conductivity is 135

or more pmhoes, and the carbon black pigment processed in Pori (1-vinyl pyrrolidone-KO-2-dimethylaminoethyl methacrylate) was able to obtain the ink of 25mgCCA content from the above-mentioned experimental result per 1g of pigments.

[0166] (Example 4) The carbon black pigment (20.0g, Monarch120 and lot 485-732, and Carbot) was added to the Pori (vinyl pyrrolidone-KO-vinyl acetate) solution (100.0g, PVP/VAE-335, the 0.67wt% solution in denatured alcohol, ISP Technologies Inc.).

[0167] The above-mentioned mixture was made to homogenize for about 10 minutes with the distributed equipment for the poly TRON laboratories, and carbon black dispersion liquid were obtained. The mixed weight ratio of a pigment and a polymer was 30:1 in these carbon black dispersion liquid.

[0168] After putting the above-mentioned black dispersion liquid into the aluminum pan and drying this at 80 degrees C for about 20 hours, disintegration was carried out using the mortar for laboratories, and the pestle, and MONAKU 120 pigment by which Pori (vinyl pyrrolidone-KO-vinyl acetate) processing was carried out was obtained.

[0169] The organosol / charge modifier / NORUPA premix (trade name) added Zr HEKISEMU solution (14.20g, 0.15wt%, OMG Americas Inc.) and NORUPA 12 (trade name) (951.8g) to organosol EHMA/HEMA-TMI///MMA/EA 1034. zero g), and vibrated these mixture for about 30 minutes using the shaker for laboratories.

[0170] 0. The IGARA cisele of 5L was filled up with POTTASU glass bead 390g, an organosol / charge modifier / NORUPA premix (trade name) 294.9g, and 5.31g of MONAKU 120 pigments by which Pori (vinyl pyrrolidone-KO-vinyl acetate) processing was carried out. The black ink of 25mg (CCA) content of charge modifiers per 1g of pigments which mills the above-mentioned constituent for 90 minutes by 2000rpm, and does not have Pori (vinyl pyrrolidone-KO-vinyl acetate) was obtained.

[0171] The particle magnitude and conductivity of black ink were measured by the above-mentioned approach.

[0172] As a result of measurement, the conductivity of 3wt% black ink was 145 pmho/cm, free phase conductivity was 5.77 pmho/cm (free 4.7% phase conductivity), and volume average particle magnitude (Horiba910) was 1.04 micrometers. Distribution of particle magnitude showed the mono-mode.

[0173] It is effective for making the charge organization potency force of a pigment improve, conductivity is 135 or more pmhoes, and the carbon black pigment processed in Pori (vinyl pyrrolidone-KO-vinyl acetate) was able to obtain the ink of a CCA25mg content from the above-mentioned experimental result per 1g of pigments. If the carbon black pigment processed from this example in order to make conductivity improve was used, when milling this under the above-mentioned conditions, not making toner particle magnitude increase compared with an unsettled black pigment will have been recognized.

[0174] (Example 5) Toluene 210g, styrene (Aldrich Chemical Company) 72.0g, dimethylaminoethyl methacrylate (Aldrich Chemical Company), g [28.0] and 2, and 2'-azo-isobutyro-dinitrile (azobisisobutironitoriru, Aldrich Chemical Company) 1.35g was put into the transparent carboy. Thus, the obtained solution was purged for 10 minutes with nitrogen gas, and it was made to arrange in the tumbler with which it was equipped with the ebullition cistern (Lauder-O-meter and Atlas Electric Products) adjusted by 70 degrees C.

[0175] After making it react at 70 degrees C, carrying out the tumbler of the above-mentioned mixture for 16 hours, it took out from the tumbler and was made to cool at a room temperature. Subsequently, they are styrene 72.0g, dimethylaminoethyl methacrylate 28.0g, and azobisisobutironitoriru to a reaction mixture. After adding 1.35g further and purging nitrogen again here, the tumbling was carried out at 70 degrees C for 20 hours. In this way, the precipitate of the opaque viscous liquid gestalt which fills about 3500ml heptane with the toluene solution of the obtained polymer, and has a ***** resemblance paste was obtained. Subsequently, the heptane was moved from the precipitate polymer and the polymer was dried for two days in the oven which has an exhaust port.

[0176] After melting the dried glassiness polymer in toluene, it was made to move and dry like these sediment formation fault twice repeatedly, and styrene / dimethylaminoethyl methacrylate mole ratio (calculated value) obtained the Pori (styrene-KO-dimethylaminoethyl methacrylate) glassiness solid-state product of 8:2.

[0177] Then, the carbon black pigment (20.0g, Monach120 and lot 485-732, and Carbot) was paid to 100g of acetone solutions of 2.0wt% Pori (styrene-KO-dimethylaminoethyl methacrylate).

[0178] The above-mentioned mixture was made to homogenize for about 10 minutes using the distributed equipment for the poly TRON laboratories, and black dispersion liquid were obtained. The mixed weight ratio of a pigment and a polymer was 10:1 in these black dispersion liquid.

[0179] After pouring the above-mentioned black dispersion liquid into 2,600g of deionized water agitated with the stirrer for laboratories gradually, agitating a reaction mixture was continued for 30 minutes. The pigment dispersion liquid in deionized water were filtered through filtration paper (Whatman#54), and it washed twice by about 150g deionized water.

[0180] After drying the pigment collected according to the above-mentioned process at 80 degrees C for 20 hours, MONAKU 120 pigment by which was made to carry out disintegration by hand using the mortar for laboratories and a pestle, and Pori (styrene-KO-dimethylaminoethyl methacrylate) processing was carried out was obtained.

[0181] The organosol / charge modifier / NORUPA premix (trade name) added Zr HEKISEMU solution (14.20g, 5.15wt%, OMG Americas Inc.) and NORUPA 12 (trade name) (951.8g) to organosol EHMA/HEMA-TMI///MMA/EA (1034. zero g), and vibrated these mixture for about 30 minutes using the shaker for laboratories.

[0182] 0. The IGARA cisele of 5L was filled up with POTTASU glass bead 390g, an organosol / charge modifier / NORUPA premix (trade name) 294.9g, and 5.65g of MONAKU 120 pigments by which Pori (styrene-KO-dimethylaminoethyl methacrylate) processing was carried out. The black ink of 25mg (CCA) content of charge modifiers per 1g of pigments which mills the above-mentioned constituent for 90 minutes by 2000rpm, and does not have Pori (styrene-KO-dimethylaminoethyl methacrylate) was obtained.

[0183] The particle magnitude and conductivity of black ink were measured by the above-mentioned approach.

[0184] As a result of measurement, the conductivity of 3wt% black ink was 135 pmho/cm, free phase conductivity was 5.12 pmho/cm (free 3.8% phase conductivity), and volume average particle magnitude (Horiba910) was 0.86 micrometers. Distribution of particle magnitude showed the mono-mode.

[0185] It is effective for making the charge organization potency force of a pigment improve, conductivity is 135 or more pmhoes, and the carbon black pigment processed in Pori (styrene-KO-dimethylaminoethyl methacrylate) was able to obtain the ink of a CCA25mg content from the above-mentioned experimental result per 1g of pigments. When milling under the above-mentioned conditions, toner particle magnitude is not made to increase compared with an unsettled black pigment, if the carbon black pigment processed from this example in order to make conductivity improve is used.

[0186] As mentioned above, although the gestalt of the suitable operation concerning this invention was explained, this invention is not limited to this configuration. If it is this contractor, various kinds of examples of correction and examples of modification can be assumed within the limits of the technical thought indicated by the claim, and it will be understood as what is included also about those examples of correction, and the example of modification by the technical range of this invention.

[Translation done.]